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TOXIC SUBSTANCE REMOVAL IN ACTIVATED SLUDGE AND PAC TREATMENT SYSTEMS

by

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The effectiveness of adding powdered activated carbon to activated sludge systems was evaluated for enhanced removal of specific toxic organic compounds. Nine organic compounds encompassing a range of solubility, volatility, biodegradability, and adsorptive properties were studied along with selected commercial powdered activated carbons. The studies showed that the addition of less than 100 mg/l powdered activated carbon did not enhance the removal of the biodegradable compounds benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, and nitrobenzene. Significantly improved removals of the poorly degradable and non-biodegradable compounds 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane, occurred at influent powdered carbon concentrations in the 12.5- to 25-mg/l range. Influent powdered carbon concentrations of 100 mg/l effected overall removals of greater than 90%. The addition of powdered activated carbon not only reduced effluent concentrations but also reduced the amounts of the volatile compounds stripped to the atmosphere.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation'a water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the use community.

The project described in this report examines the fate of toxic substances in conventional wastewater treatment systems, and evaluates methods for enhancing the removal of toxic compounds in such systems. As such, it addresses the issues of treatment of municipal and industrial wastewater discharges as well as the control of releases of toxic substances to the environment.

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

The effectiveness of adding powdered activated carbon to activated sludge systems was evaluated for enhanced removal of specific toxic organic compounds. Little prior information existed on the behavior of toxic organics during activated sludge treatment. Thus a considerable effort was directed toward identifying and quantifying the fate of specific compounds in conventional activated sludge systems as well as in those to which carbon was added. Nine organic compounds encompassing a range of solubility, volatility, biodegradability, and adsorptive properties were studied along with selected commercial powdered activated carbons recommended for use in integrated activated sludge/carbon treatment systems. Completely-mixed-flow bioreactors equipped with internal clarifiers and air-tight lids were used to study the removal of each compound. Completely-mixed batch rate and equilibrium studies were conducted to quantify the removal mechanisms -- volatilization, biodegradation, biosorption, and carbon adsorption.

Results from steady-state bioreactor studies showed that the addition of less than 100 mg/l powdered activated carbon did not enhance the removal of the biodegradable toxics benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, and nitrobenzene. Significantly improved removals of the poorly degradable and nonbiodegradable compounds 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane occurred at influent powdered carbon concentrations in the 12.5- to 25-mg/l range. Influent powdered carbon concentrations of 100 mg/l effected overall removals of greater than 90%. The addition of powdered activated carbon not only reduced effluent concentrations but also reduced the amounts of the volatile compounds stripped to the atmosphere.

This report was submitted in fulfillment of Contract No. CR 806030 by The University of Michigan under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 9/1/80 to 2/28/83, and work was completed as of 2/28/83.

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ABBREVIATIONS AND SYMBOLS

B	empirical volatilization constant (dimensionless)
BOD	biological oxygen demand (M/L^3)
C or C_e	aqueous effluent concentration (M/L^3)
C_g	off-gas concentration (M/L^3)
C_o or C_i	aqueous influent concentration (M/L^3)
C_s	waste sludge concentration (M/L^3)
COD	chemical oxygen demand (M/L^3)
D	diffusivity (L^2/T)
f_b	fraction of influent biodegraded
f_e	fraction of influent present in the effluent
f_v	fraction of influent volatilized
H	Henry's Constant (L^3atm/mol)
k_b	pseudo first order biodegradation rate coefficient (1/T)
k_g	gas phase mass transfer coefficient (L/T)
k_L	liquid phase mass transfer coefficient (L/T)
k_La	oxygen reaeration rate coefficient (1/T)
k_o	overall pseudo first order removal coefficient (1/T)
k_v	first order volatilization rate coefficient
$k_{v,o}$	empirical volatilization coefficient (1/T)
K_B	bioconcentration factor (dimensionless)
K_f	Freundlich adsorption constant
K_{OL}	overall mass transfer coefficient (L/T)
K_{ow}	octanol water partition coefficient (dimensionless)
K_p	linear partition coefficient (L^3/M)
L	empirical volatilization proportionality coefficient (L^{-3})
M_s	concentration of biological solids (M/L^3)
MLSS	mixed liquor suspended solids concentration (M/L^3)

N_e	mass flux of a compound out of a bioreactor (M/T)
N_g	mass flux of a compound in the off-gas (M/T)
N_o	mass flux of a compound into a bioreactor (M/T)
N/N_o	fractional recovery of a compound in the experimental system (dimensionless)
n	Freundlich adsorption constant
P	pressure (atm)
Q_a	influent aeration rate (L^3/T)
Q_e	effluent aqueous flow rate (L^3/T)
Q_i	influent aqueous flow rate (L^3/T)
Q_g	off-gas flow rate (L^3/T)
Q_s	solids waste rate (L^3/T)
q_e	solid phase concentration of a compound (M/M)
R	universal gas constant ($ML^2/T^2/{}^oK$)
r	resistance to mass transfer (T/L)
S	empirical reaeration rate proportionality constant
SRT	solids retention time (T)
t	time (T)
$\bar{t}$	hydraulic retention time (T)
T	temperature (^oC)
TOC	total organic carbon concentration (M/L^3)
V	volume (L^3)
V_g	volume of gaseous phase (L^3)

SECTION 1

INTRODUCTION

The presence of toxic organic compounds in natural water systems and drinking water supplies has significantly modified the emphasis of wastewater treatment during the past several decades. Wastewater treatment systems have been designed to remove the traditionally regulated pollutants such as BOD, suspended solids, pathogenic organisms, and possibly nitrogen and phosphorus; but the removal of these substances alone is no longer sufficient to protect the quality of receiving waters. Future discharge regulations are likely to impose limitations on specific toxic substances such as the 114 organic compounds designated as priority pollutants by the U.S. Environmental Protection Agency (EPA).

The presence of toxic organic compounds in municipal and industrial wastewaters necessitates an understanding of the capabilities of conventional wastewater treatment systems for removing such substances. Some of the toxic organic compounds are adequately removed, but the specific removal mechanisms for those substances must be identified and quantified so that treatment systems can be operated to achieve maximum removals. Other compounds are not removed to levels considered acceptable for discharge; treatment of these substances will require modifications of or alternatives to existing waste treatment systems.

Little information is available on the fate of specific toxic organic compounds during conventional wastewater treatment. Four mechanisms control their removal during conventional treatment: chemical transformations, volatilization, biodegradation, and bioaccumulation or biosorption. Current knowledge about the role of each mechanism and their interactions with regard to trace toxic organics removal is insufficient to develop treatability models that explain the behavior of those substances during treatment.

Various modifications of and alternatives to conventional biological treatment processes have been suggested and evaluated in bench-, pilot-, and full-scale treatment systems during the past several decades. The addition of powdered activated carbon (PAC) to the aeration basins of existing activated sludge facilities has emerged as an attractive application of carbon adsorption technology to toxic organics removal. The integrated process using activated sludge and carbon (also known as PACT®) was originally introduced as a method for upgrading activated sludge waste treatment in removing conventional pollutants. The process's ability to provide enhanced removal of toxic organic compounds may be more significant. Only a few studies have detailed the removal of toxic organics in such integrated systems. Little direct information exists on either the fate of specific toxic compounds during integrated activated sludge/carbon treatment or on the factors that control the effectiveness of PAC addition to activated sludge for removing toxic organics from wastewaters.

This project was designed to study the effectiveness of adding PAC to activated sludge systems for providing enhanced removal of specific toxic organic compounds. Completely-mixed-flow (CMF) biological reactors were used to study the integrated PACT® process. The effectiveness of the integrated system was evaluated by comparing removals of the toxic organic compounds in parallel, control-activated sludge bioreactors and activated sludge bioreactors receiving slurried, powdered activated carbon. Since little information exists on the behavior of toxic organics during activated sludge treatment, a major portion of this project was directed toward identifying and quantifying the fate of each test compound in conventional activated sludge systems. Major operating parameters that were studied under steady-state operating conditions included carbon type and concentration, solids retention time, concentration of the toxic substance(s), hydraulic retention time, and organic composition and concentration of the wastewater.

A secondary objective of the project was the quantification of the mechanisms effecting removal of toxic organic compounds during activated sludge treatment and integrated activated sludge and carbon treatment. Three removal mechanisms are important during activated sludge treatment; volatilization, biosorption, and biodegradation. The addition of PAC provides carbon adsorption as a fourth significant removal mechanism in integrated systems. Completely-mixed batch rate and equilibrium studies were used to quantify each removal mechanism to develop a steady-state trace organics removal model.

SECTION 2

CONCLUSIONS

This study has provided important information concerning the removal of toxic organic compounds during activated sludge treatment and integrated activated sludge and carbon treatment. Four removal mechanisms were identified as affecting the fate of the compounds during treatment: volatilization, biodegradation, biosorption, and powdered carbon adsorption. The study demonstrates the importance of using CMF bioreactors designed to enable collection and analysis of off-gases for evaluating the fate of specific volatile compounds, both biodegradable and nonbiodegradable.

The results indicated that conventional activated sludge systems can acclimate to and hence effect significant reductions in both effluent and off-gas concentrations of the toxic organic compounds at microgram-per-liter concentrations. Overall reductions in effluent and off-gas concentrations resulting from biodegradation averaged 75% to 85% for the volatile compounds benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene under steady-state operating conditions. Acclimation periods ranged from 7 to 14 days.

The addition of PAC provided enhanced removals of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane. Powdered carbon addition effected reductions in both the effluent and off-gas concentrations of volatile, nonbiodegradable compounds. PAC doses as small as 25 to 50 mg/ℓ produced significant improvements in nonbiodegradable toxics removal compared with control activated sludge systems. Greater than 90% removals occurred at influent carbon doses of 100 mg/ℓ. The addition of PAC at influent doses less than 100 mg/ℓ did not enhance the removal of the biodegradable toxic organics.

PAC bioreactor studies conducted at solids retention times (SRT's) of 0.25 to 12 days and a 50-mg/ℓ carbon dose showed that the removal of nonbiodegradable toxics was the same over the range of SRT's studied. The most important operating parameter with respect to removals of toxics was the influent PAC concentration.

Results from this study showed that the proposed steady-state trace organics removal model (STORM) could be used to describe adequately the fate of each organic compound in the activated sludge bioreactors. Mass balance determinations showed that PAC adsorption in the integrated activated sludge and carbon treatment system could not be modeled based on equilibrium considerations.

SECTION 3

RECOMMENDATIONS

This study has laid a strong foundation in the overall assessment of the fate and behavior of specific categories of organic priority pollutants in a conventional and an advanced wastewater treatment system. Additional research is needed to build on this foundation to define the capabilities and limitations of conventional and alternative wastewater treatment systems for providing sufficient removal of toxic materials to protect the integrity of water courses and drinking water supplies. Outlined below are specific recommendations for future research:

1) Investigate the fate and behavior of additional categories of toxic organic compounds in conventional wastewater treatment systems. Studies should be conducted at enviromentally realistic wastewater concentrations, and treatment systems should be designed to facilitate mass balance determinations.

2) Conduct activated sludge studies with actual municipal wastewater to evaluate the effect of background solution on biodegradation of trace levels of organic compounds.

3) Specifically evaluate the effect of influent concentrations on biodegradation rates of additional compounds.

4) Examine the biodegradation potential of trace organic priority pollutants as a function of the type of wastewater treatment process. Studies should include trickling filters, rotating biological contactors, anaerobic digesters, etc.

SECTION 4

BACKGROUND

4.1 OCCURRENCE OF TOXIC ORGANIC COMPOUNDS IN WASTEWATER

Information regarding the numbers and concentrations of toxic organic compounds being discharged from wastewater treatment facilities before the mid-1970's was limited. Prior to the adoption of the Water Pollution Control Act Amendments (PL92-500) in 1972, concern about wastewater discharges focused on the conventional pollutants such as BOD, suspended solids, pathogenic organisms, oil and grease, nitrogen and phosphorus. The assimilative capacities of receiving streams was considered in the formulation of effluent standards for pollutants such as BOD and suspended solids. In 1972 the EPA was required by PL 92-500 to formulate national discharge regulations for municipal and industrial wastewater treatment facilities and to establish a list of toxic compounds for development of specific discharge standards. The resulting "Priority Pollutant List" contained 114 toxic organic compounds, 13 metals, and cyanide and asbestos (1).

A number of studies have been conducted during the past several years to evaluate the presence and behavior of toxic organics in conventional wastewater treatment facilities (1,2,3). The majority of these studies focused on the identification and quantification of specific compounds. An investigation of fifty municipal wastewater treatment facilities found a total of 88 different organic priority pollutants in influents and 76 organic priority pollutants in effluents at least once (2). The major findings of this study were:

-The larger the industrial contribution to a Publicly Owned Treatment Works (POTW), the higher the concentration of priority pollutants in the POTW influents

-50% of the secondary treatment plants achieved minimum organic removals of 82% for volatiles and 65% for base/neutral extractables

-tertiary treatment processes effected greater removals of priority pollutants than secondary processes

-primary treatment was less effective than either secondary or tertiary processes in removing priority pollutants

-mass loadings of priority pollutants were higher on weekdays than on weekends

-in general, as influent concentrations increased, effluent concentrations also increased implying that the removal rates for priority pollutants were relatively constant.

A thirty consecutive day study of one activated sludge treatment facility found a total of 58 toxic organics in the influent and 40 toxic organics in the effluent at least once (3). Average removals of organic priority pollutants were reported as 95% for volatiles, 87% for base/neutral extractables, and 77% for acid extractables. The major findings of the thirty-day study were (3):

-by-products from industrial processes were the primary sources of priority pollutants in the influent

-primary treatment did not provide significant removals of priority pollutants, ranging from less than 20% for volatiles to no removal of acid and base/neutral extractables

-secondary treatment provided the most significant removals of all classes of organic priority pollutants

-bio-floc adsorption was the primary removal mechanism for acid and base/neutral extractables

-increases in influent concentrations resulted in corresponding increases in effluent concentrations

-regression analysis between the most frequently occurring priority pollutants and two conventional pollutants, BOD5 and TSS were not indicative of the levels of toxic pollutants in the secondary effluent

A recent study of the wastewater treatment facilities of five organic chemical manufacturing plants found that conventional activated sludge treatment provides removals of most organic priority pollutants sufficient to produce effluent concentrations of 10 parts-per-billion or less (4).

One of the conclusions of the five-plant survey was that while no reliable correlation existed between conventional and non-conventional pollutants and toxic organic compounds, to a limited extent it may be possible to utilize selected toxic organic compounds as indicators of the removal of other organic compounds with similar biotreatability properties.

While such studies have contributed important information on the removals of toxic organic compounds by conventional wastewater treatment systems, they have not provided insight into the role of specific removal mechanisms.

4.2 INTEGRATED ACTIVATED SLUDGE/CARBON TREATMENT

4.2.1 Background

Interest in the applications of carbon adsorption technology to wastewater treatment began in the late 1950's under the Advanced Waste Treatment Research (AWTR) Program of the U. S. Public Health Service. The program was developed to investigate various types of physicochemical processes to remove the increasing numbers of recalcitrant synthetic compounds causing pollution of water systems and drinking water supplies (5). Adsorption by granular activated carbon (GAC) was demonstrated to be an effective method of removing a broad spectrum of organic compounds of concern during extensive studies of physicochemical treatment systems in the 1960's and 1970's. The most effective applications of GAC treatment were in a tertiary mode following secondary biological systems for providing advanced waste treatment (5-13). Granular activated carbon in tertiary treatment systems functions to reduce the overall organic content of the wastewater by removing biologically resistant compounds. A major factor that limited the use of GAC tertiary systems was the large capital costs associated with installing and maintaining such systems. Capital and operating costs for tertiary GAC adsorption systems with carbon regeneration facilities can equal or exceed the costs of the entire activated sludge process. Additionally, land requirements of tertiary systems often can make their implementation impossible.

Independent physicochemical treatment (IPCT) of clarified raw wastewater has been investigated as an alternative to secondary biological treatment followed by a tertiary GAC adsorption system (6-21). Major problems associated with independent physicochemical treatment systems have been their inability to remove biodegradable, low molecular weight compounds which exert a BOD in the wastewater effluent, and excessive odor generation resulting in high operating costs to overcome it.

An attractive alternative use of activated carbon in wastewater treatment is the integrated activated sludge/carbon treatment system. In this process, powdered activated carbon (PAC) is added in a slurried form directly to the aeration basin of an activated sludge facility. A schematic illustration of this process is presented in Figure 4-1. Once introduced into the aeration basin the PAC is rapidly incorporated into the biological flocs of the activated sludge forming a matrix of activated carbon and biomass. The residence time of the PAC in the aeration basin is the mean solids retention time of the biological solids. Integrated activated sludge/carbon treatment systems combine the synergistic interactions of biodegradation and carbon adsorption to achieve effluent qualities comparable to or better than secondary biological treatment followed by tertiary physicochemical treatment with granular carbon adsorption. Low molecular weight organics not amenable to carbon adsorption are removed through biodegradation while larger, more complex molecules which are not biodegradable are removed by adsorption onto the powdered activated carbon.

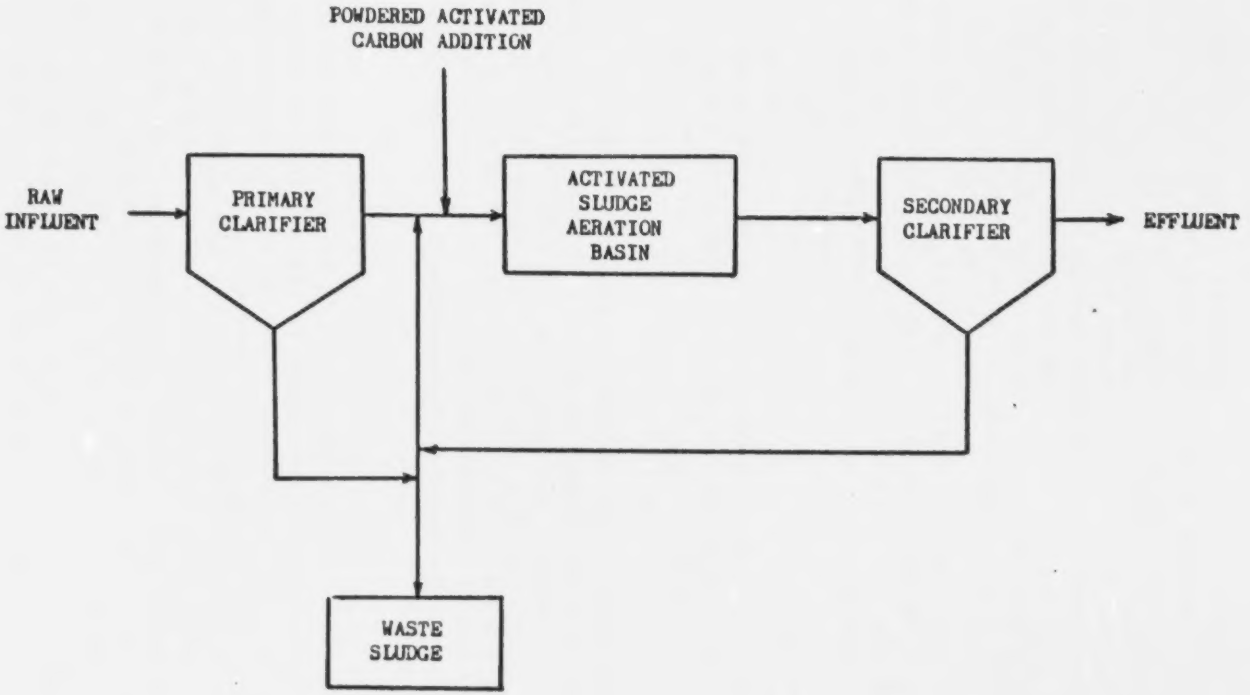

POWDERED ACTIVATED
CARBON ADDITION
RAW
INFLUENT
PRIMARY
CLARIFIER
ACTIVATED
SLUDGE
AERATION
BASIN
SECONDARY
CLARIFIER
EFFLUENT
WASTE
SLUDGE

FIGURE 4-1. Simplified schematic diagram of the PACT® system.

An attractive feature of the integrated activated sludge/carbon treatment system is the ease with which it can be adapted to existing activated sludge plants. The addition of PAC to activated sludge has been demonstrated as a viable method of improving the performance of biological wastewater treatment with respect to improved (22-35):

- organics removal measured as BOD, COD, and/or TOC;
- color removal;
- process stability;
- hydraulic capacity;
- oxygen transfer;
- resistance to shock loadings;
- low temperature performance;
- sludge settleability, thickening, and dewatering;
- anaerobic digestion;
- nitrification;
- toxic organic removal.

The concept of adding PAC to activated sludge was originally introduced as a method of improving the performance of existing activated sludge with respect to the reduction of overall organics expressed as BOD, COD and/or TOC. Addition of PAC to activated sludge was first investigated nearly fifty years ago in an effort to improve performance of overloaded sewage plants (35). The process was largely ignored until the early 1970's when more stringent discharge regulations required advanced wastewater treatment to remove refractory organic compounds.

Improved performance of activated sludge processes by the addition of PAC has been reported for a variety of municipal and industrial wastes. The most thoroughly studied full-scale use of the PACT^{R} process has been at the DuPont Corporation's Chambers Works organic chemicals manufacturing facility where much of the development work on the process was conducted (27, 30, 31, 33). It was the first full-scale modification of activated sludge treatment by PAC-addition. An influent

PAC dose of approximately 130 mg/l has been used with a 45-day sludge age to successfully treat a 40 mgd complex wastewater since the mid 1970's.

4.2.2. Toxic Organics Removal

While the effectiveness of adding PAC to activated sludge for improved process performance with respect to conventional pollutants has been well documented, there have been only a limited number of studies on the removal of toxic organics in PACT® systems. These studies have focused on the effect of PAC-addition for enhanced toxics removal from industrial wastes (40-44).

Hutton and Temple (41) and Hutton (42) reported on the removals of specific priority pollutants from the full-scale 40 mgd PACT Chambers Works facility treating a complex waste from an organic chemical manufacturing industry. The influent PAC concentration was given as 134 mg/l of which 68% was virgin produced carbon and 32% was regenerated carbon. Results from that study indicated removals of all but four compounds exceed 90%.

Hutton and Temple (41) also reported on bench scale studies of parallel activated sludge and PACT® treatment systems of toxic organic removals. The results from their study showed that removals of volatile organics from activated sludge reactors were in excess of 96% and that the addition of 100 and 300 mg/l PAC to the influent produced no additional removals. Removals of less volatile base/neutral and acid extractable compounds were significantly improved by the addition of 100 and 300 mg/l PAC. Results presented by Hutton and Temple (41) indicated that PAC-addition to activated sludge reduced the effluent concentrations of non-volatile, non-biodegradable compounds. A significant aspect of the results reported by Hutton (42) was the ability of PAC to adsorb toxic pollutants present at trace concentrations from a complex background solution. Hutton (42) reported that the sum of all of the priority pollutants constituted less than 5% of the total dissolved organic carbon present in the wastewater.

Another study by Hutton (43) compared the removal of specific organic priority pollutants by PACT® activated sludge to conventional activated sludge followed by a tertiary GAC adsorption system. Activated sludge alone produced at least 85% removal of 23 of the 36 toxic organics detected in the influent. Compounds exhibiting the greatest removal were also the most volatile. The addition of 100 mg/l PAC to the influent increased performance so that greater than 85% removal was obtained for 30 of the 36 compounds. Results from the tertiary GAC column studies showed an interesting chromatographic effect in which the concentrations of twelve compounds were larger in the column effluents than in the feed for a period of time. At the point of TOC and color breakthrough Hutton (43) reported that only 11 of the 36 compounds had removals greater than 85% and 17 were removed by 50% or greater. A conclusion of this study was that PAC addition to activated sludge provided superior removals of organic priority pollutants compared to activated sludge followed by tertiary GAC adsorption.

Kincannon and Esfandi(44) reported on the removals of organic priority pollutants in a pilot plant study of the PAC/activated sludge process for treating pharmaceutical manufacturing wastes. A comparison of the removals of the toxic organic compounds from an activated sludge system and a PACT® activated sludge system receiving an influent PAC concentration of 347 mg/l showed that the addition of PAC provided better removals of the toxic organics when average effluents concentrations were compared. Comparisons of the daily values reported by the authors showed that in many cases the activated sludge was able to achieve treatment levels comparable to the system with PAC. The primary benefit of adding PAC was reported to be enhanced toxics removal that occurred during periods of shock loadings when removals in the activated sludge system decreased. The shock loadings had no apparent effect on the performance of the PACT® activated sludge system with respect to the removal of the toxic organics.

SECTION 5

EXPERIMENTAL DESIGN

This section reviews 1) the selection of the toxic organic compounds and powdered activated carbons, 2) the design of the experimental systems used to study the fate of the compounds in continuous flow activated sludge and integrated activated sludge/carbon treatment systems, and 3) the experimental methodologies used to conduct the various equilibrium and rate experiments designed to study individual removal mechanisms of volatilization, biodegradation, biosorption, and carbon adsorption.

5.1. SELECTION OF TOXIC ORGANIC COMPOUNDS

Nine specific organic compounds were included in the study. These compounds, presented with pertinent physical properties in Table 5-1, encompass a broad range of volatility, biodegradability and adsorptive properties. All of the compounds except o-xylene are included in the EPA list of Priority Pollutants. An important and unique feature of this study was the use of toxic pollutants known to be present in wastewaters and at concentrations representative of those actually found in municipal and industrial wastewaters. Influent concentrations used in the bioreactor studies primarily were in the 50 to 200 μg/l range.

5.2. SELECTION OF POWDERED ACTIVATED CARBONS

Background adsorption studies were conducted with a variety of adsorbents to select a powdered activated carbon as the primary adsorbent to be used in the continuous-flow bioreactor studies. The initial studies considered a total of five adsorbents; three of which were powdered activated carbons, one was a powdered form of a granular carbon, and the last was a non-activated carbonaceous material. A summary of the pertinent properties of each adsorbent is given in Table 5-2.

The powdered activated carbons Hydrodarco C and SA-15 are recommended by their manufacturers for use in the PACT® process. Amoco's PX-21 is an experimental powdered activated carbon with a very high surface area. Based upon adsorptive performance in equilibrium studies and commercial availability for wastewater treatment Hydrodarco C was chosen as the primary adsorbent for the bioreactor studies.

TABLE 5-1

PHYSICAL PROPERTIES OF
TOXIC ORGANIC COMPOUNDS

Compound	Solubility (mg/l)	Vapor Pressure (atm)	Henry's Constant (m^3atm/mol x 10^{-3})	Log Octanol/ Water Partition Coefficient
		Purgeable		
1. Benzene	1750	0.125	5.49	1.95
2. Toluene	534	0.0374	6.66	2.69
3. Ethylbenzene	152	0.0125	8.73	3.15
4. o-Xylene	175	0.00868	5.27	3.12
5. Chlorobenzene	488	0.01382	3.71	2.84
		Base Neutral Extractable		
6. 1,2-Dichlorobenzene	145	$1.32x10^{-3}$	2.96	3.38
7. 1,2,4-Trichlorobenzene	30	$5.53x10^{-4}$	2.32	4.26
8. Nitrobenzene	1900	$1.97x10^{-4}$	0.023	1.85
		Pesticide		
9. Lindane	7.3	$4.34x10^{-7}$	0.00043	3.72

TABLE 5-2

PHYSICAL PROPERTIES OF ACTIVATED CARBONS

Carbon Type	Manufacturer	Surface Area, BET (m^2/gm)	Iodine No. (mg/gm)	Base Material
Hydrodarco C [1]	ICI, Americas	550	N.A.	Lignite
Nuchar SA-15 [1]	Westvaco	1400 - 1800	80	Bituminous Coal
PX-21 [2]	Amoco	2800 - 3500	2800 - 3600	N.A.
Filtrasorb 400 [3]	Calgon	1050 - 1200	1000	Bituminous Coal
Anthrafilt [4]	Unifilt	N.A.	N.A.	Anthracite Coal

N.A. Not Available

[1] Recommended by manufacturer for PACT process

[2] Experimental PAC

[3] Powdered version of this granular activated carbon

[4] Non-activated carbonaceous material

5.3. BIOREACTOR DESIGN

Completely-mixed flow (CMF) bioreactors were used to study the fate of the toxic organic compounds during activated sludge and integrated activated sludge/carbon treatment processes. A variety of laboratory-scale CMF reactors have been used in both activated sludge and PAC addition to activated sludge studies. Bioreactors for this project were designed to satisfy the following criteria:

-provide adequate mixing to be modelled as a CMF reactor;

-enable collection of volatilized organics in off-gases;

-contain an internal clarification unit to control solids retention time;

-be small enough to permit ease of handling;

-be constructed readily and economically.

Two different reactor configurations were employed during the project. A 10-liter bioreactor was used for all of the studies with the synthetic wastewater, and a smaller 3-liter unit was used for studies conducted with settled primary effluent from the Ann Arbor wastewater treatment facility. Studies with the 3-liter unit were confined to the most recalcitrant compound, lindane. A description of the experimental system for each reactor configuration is presented below.

5.3.1 Bioreactor Studies Using Synthetic Wastewater

The 10-liter bioreactor design was an adaptation of the sliding baffle type CMF reactors commonly used for activated sludge studies. The bioreactors were constructed of quarter-inch plexiglass and contained 10-liter aeration sections and one-liter internal clarifiers separated by adjustable baffles. A schematic illustration of the bioreactor design is presented in Figure 5-1. Each bioreactor was fitted with an air-tight lid that covered both the aeration and clarification sections. Three stone diffusers, located at the rear of each bioreactor, supply compressed air to aerate the mixed liquor and maintain completely-mixed conditions in the aeration section.

The influent to each bioreactor was composed of three separate flows: a synthetic wastewater flow, a toxic organic solution flow, and a slurried powdered activated carbon flow. The PAC slurry was prepared with tap water and stored in well-stirred glass containers. A schematic diagram of the experimental system is shown in Figure 5-2. Bioreactors without powdered activated carbon received tap water in place of the slurried carbon flow. Individual peristaltic pumps were used to deliver the influent flows to each bioreactor from appropriate storage reservoirs allowing selected operating parameters to be varied

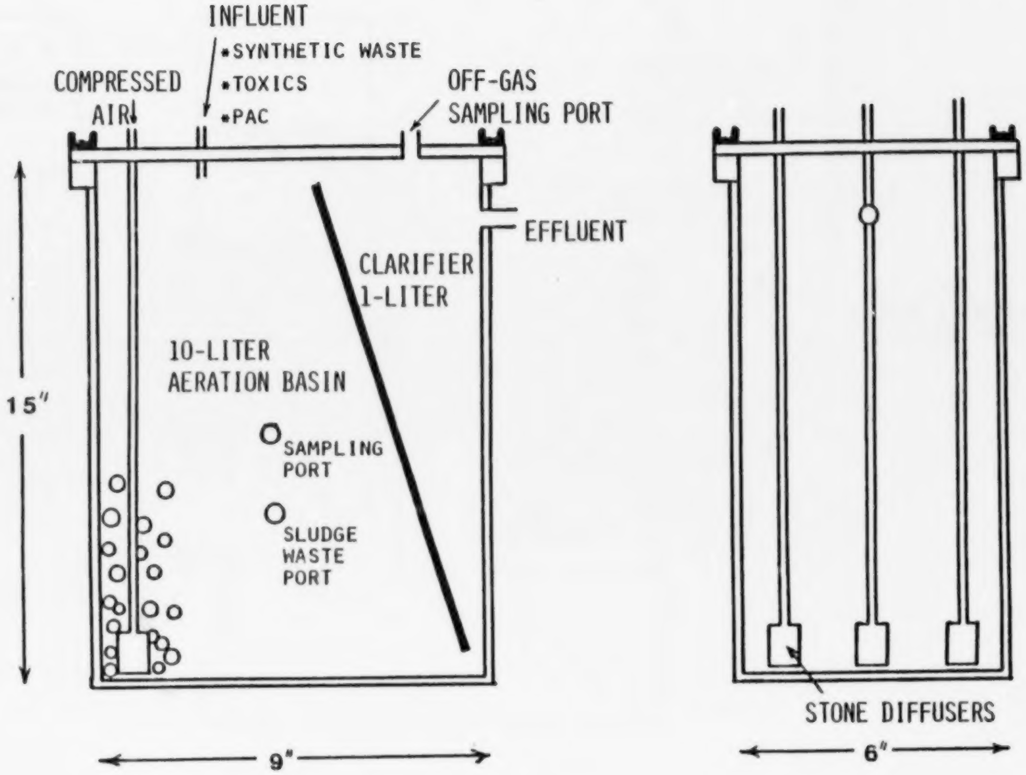

INFLUENT
*SYNTHETIC WASTE
*TOXICS
*PAC
COMPRESSED AIR
OFF-GAS SAMPLING PORT
EFFLUENT
CLARIFIER 1-LITER
10-LITER AERATION BASIN
SAMPLING PORT
SLUDGE WASTE PORT
15"
9"
STONE DIFFUSERS
6"

FIGURE 5-1. Schematic diagram of 10-liter bioreactor.

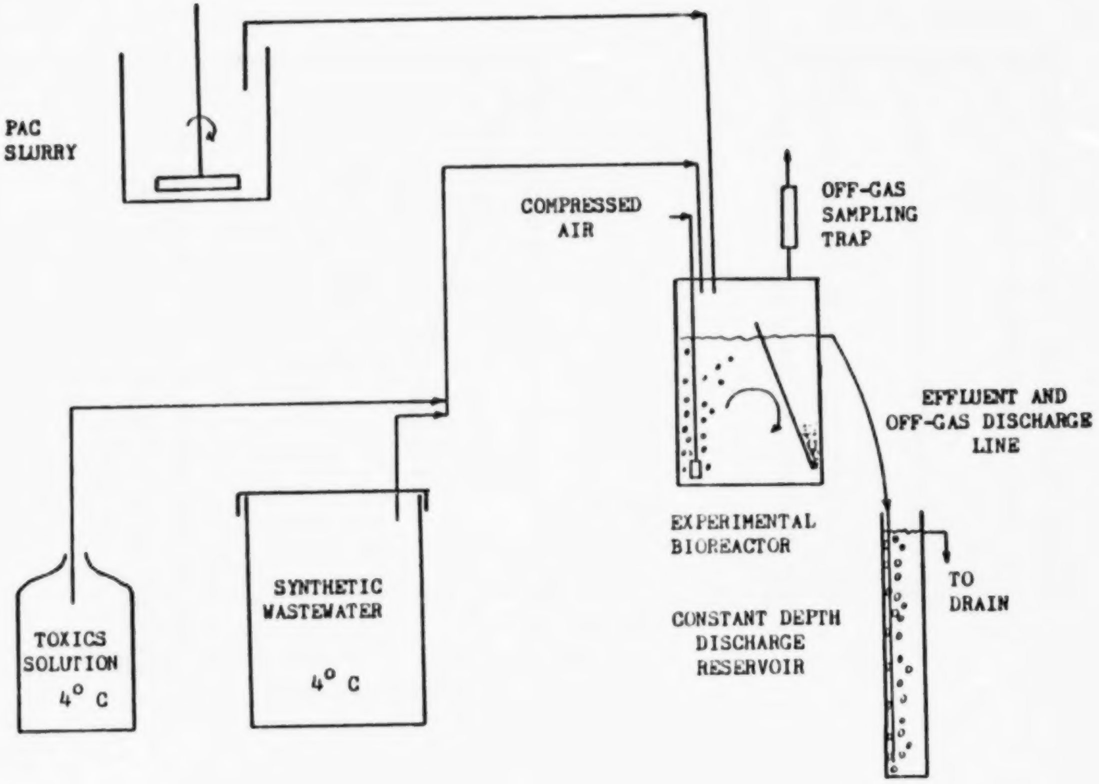

PAC
SLURRY
COMPRESSED
AIR
OFF-GAS
SAMPLING
TRAP
EFFLUENT AND
OFF-GAS DISCHARGE
LINE
EXPERIMENTAL
BIOREACTOR
CONSTANT DEPTH
DISCHARGE
RESERVOIR
TO
DRAIN
TOXICS
SOLUTION
4° C
SYNTHETIC
WASTEWATER
4° C

FIGURE 5-2. Schematic illustration of experimental system.

independently. Wastewater and toxic organic solutions were stored at 4° C to minimize biodegradation and volatilization, respectively. The mean solids retention time (SRT) was controlled by intermittently pumping a specified volume directly from the aeration section each day.

A synthetic wastewater was used to ensure adequate experimental controls on the system and to provide a common basis for data interpretation. The criteria used in the selection of the synthetic waste were that it be similar in character to domestic waste, be reproducible, and not interfere with the analyses of the toxic organic compounds. The composition of the synthetic waste is detailed in Table 5-3.

The air-tight lids were an important and unique feature of the experimental system that permitted collection and sampling of bioreactor off-gases for analysis of each toxic organic compound. Analyses of the off-gases combined with analyses of influents, effluents and waste sludges enable formulation of a mass balance for each toxic compound and determination of its fate during treatment.

5.3.2. Bioreactor Studies Using Primary Effluent

A smaller, modified version of the 10-liter bioreactors was used to study lindane removal from an integrated activated sludge/carbon treatment system receiving wastewater from the Ann Arbor treatment facility. The smaller reactors were used to reduce the volume of wastewater that had to be transported from the treatment facility to the Environmental and Water Resources Laboratory. The bioreactors were constructed of quarter-inch plexiglass and contained 3-liter aeration basins and 0.4 liter internal clarifiers separated by adjustable baffles. A schematic illustration of the 3-liter units is presented in

TABLE 5-3

SYNTHETIC FEED COMPOSITION

Compound	Percentage as TOC
Dextrin	30
Bacto Peptone	20
Sodium Acetate	15
Sodium Citrate	15
Glycine	10
Potassium Biphthalate	10
Inorganic compounds necessary for proper bacterial growth	
$NaHCO_3$ for pH control	

Figure 5-3. Two stone diffusers, located at the rear of each reactor supplied compressed air to aerate the mixed liquor and maintain completely-mixed conditions in the aeration section. Background studies showed lindane was non-volatile, therefore the reactors were not equipped for off-gas sampling.

The influent to the 3-liter reactors was composed of two separate flows: primary effluent spiked with lindane and slurried powdered activated carbon. Control activated sludge reactors received tap water instead of the powdered activated carbon. The wastewater used as feed for bioreactors was collected from the effluent of the primary settling basins every four days and stored at 4° C. Solids were wasted daily from the aeration section on a batch basis after samples for lindane analyses, TOC, and MLSS were collected.

5.4 COMPLETELY-MIXED BATCH RATE STUDIES

An integral part of this research was the quantification of the mechanisms that effected removal of toxic organic compounds from the CMF bioreactors. Batch studies were conducted to evaluate:

(1) volatilization removal rate coefficients for air stripping of volatile compounds

(2) oxygen reaeration

(3) biodegradation rate coefficients for TOC removal and toxic organics removals

(4) PAC adsorption

5.4.1. Volatilization Rate Studies

The volatilization of each toxic organic compound was studied in 10-liter bioreactors operated in batch modes to determine the first order volatilization rate coefficients for each compound. These studies were conducted in the absence of activated sludge to ensure that volatilization was the only removal mechanism. Bioreactors used to quantify volatilization were operated with air-tight lids to simulate the configuration of the CMF units. Additional volatilization studies were conducted in 10-liter bioreactors without air-tight lids to determine the effect of sealing the bioreactors upon air stripping. Volatilization rate studies were conducted at aeration rates from 1.0 to 5.0 l/min to evaluate the relationship between aeration rate and volatilization rate coefficient for each compound.

Volatilization studies were conducted by spiking the bioreactors with 20-μℓ of a methanol solution containing one or more toxic compounds to produce initial concentrations between 80 and 100 μg/ℓ. After mixing for five minutes with a magnetic stir bar, air flow was begun to the

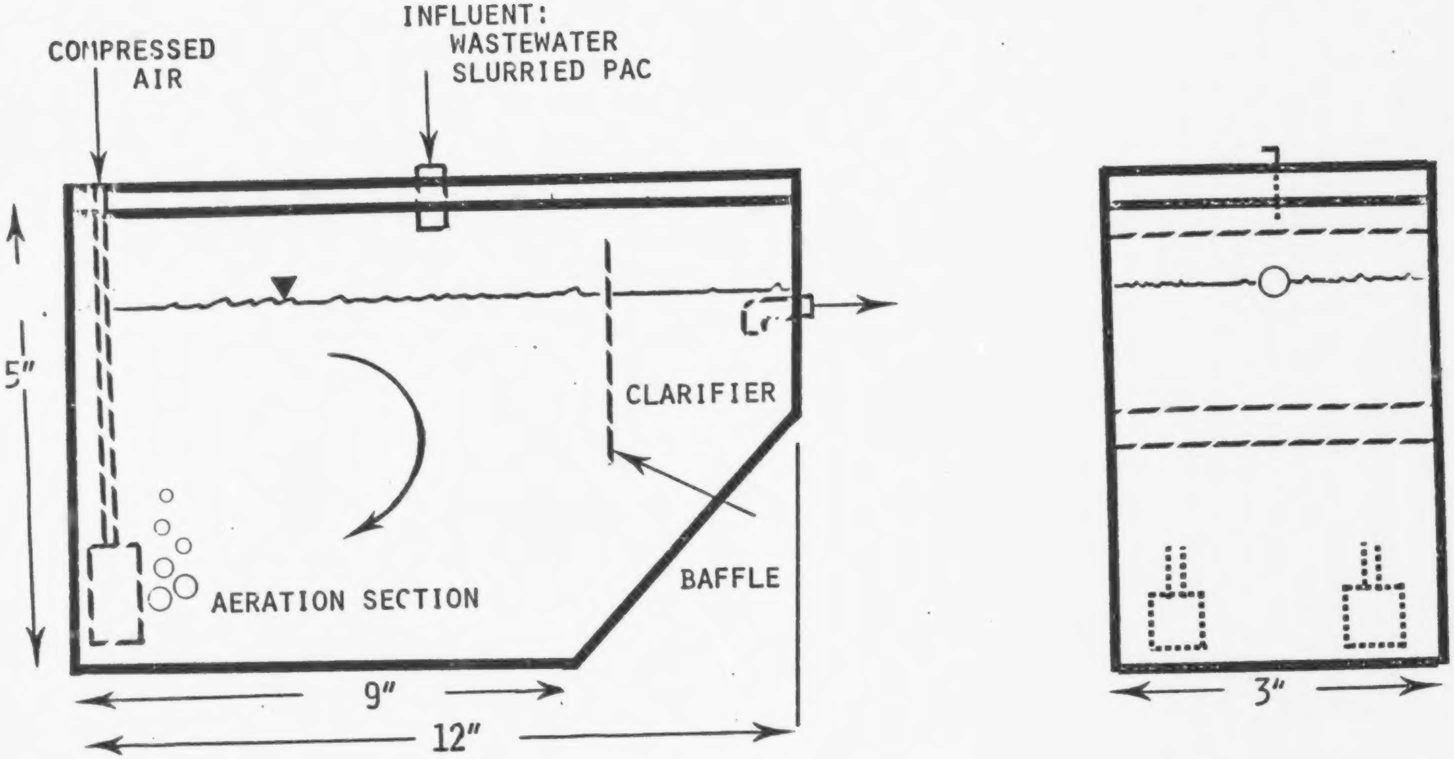

COMPRESSED AIR
INFLUENT: WASTEWATER SLURRIED PAC
CLARIFIER
BAFFLE
AERATION SECTION
5"
9"
12"
3"

FIGURE 5-3. Schematic illustration of the 3-liter bioreactor design.

bioreactors. Samples withdrawn from a sampling port on the side of each reactor were collected at specified times and analyzed for the particular compound(s) present.

5.4.2. Oxygen Reaeration Studies

Oxygen reaeration rate studies were conducted in the 10-liter bioreactors operated in batch modes in the absence of activated sludge. Reaeration studies were conducted by bubbling $N_2(g)$ through the water to reduce the dissolved oxygen concentration to less than 1.0 mg/ℓ. The bioreactors were then aerated with compressed air and the concentration of dissolved oxygen measured with an Orion dissolved oxygen probe. Data from the reaeration studies was evaluated by plotting $-\ln(C_s - C/C_s - C_o)$ versus time to determine the reaeration rate coefficients.

5.4.3. Biodegradation Rate Studies

Completely-mixed batch (CMB) rate studies were conducted to evaluate the biological degradation of overall organics as measured by soluble TOC and each of the toxic organic compounds. The TOC degradation studies were conducted in the 10-liter bioreactors used for the continuous flow studies. Prior to adding a concentrated synthetic wastewater solution to produce an initial TOC concentration of approximately 100 mg/ℓ, influent and sludge waste flows were stopped to make the bioreactors operate in batch modes. Samples were taken directly from the aeration section, filtered through Gelman A/E glass fiber filters into sample bottles, acidified with phosphoric acid, and stored at 4° C. Soluble TOC was then measured with a Dohrman model DC 80 total organic carbon analyzer.

Two types of completely-mixed batch reactor studies were conducted to investigate the biodegradation of specific volatile toxic organics observed in the CMF bioreactors. Initial CMB biodegradation studies were conducted in 2.6-liter reactors with lids to minimize volatilization. Biodegradation rate studies with volatile compounds were begun by quickly transferring 2.6 liters of activated sludge from the aeration section of a 10-liter CMF bioreactor to the glass CMB reactor and aerating it with compressed air to produce dissolved oxygen concentrations of 6 to 7 mg/ℓ. A dissolved oxygen probe was inserted through a hole in the reactor lid to continuously monitor the dissolved oxygen concentration. After the aeration was stopped the reactor was spiked immediately with 10-µℓ of a methanol solution containing the toxic compound to which the activated sludge had been acclimated. Mixing was accomplished with a teflon-coated magnetic stirring bar. Samples were withdrawn from the reactor with a 10-mℓ syringe, filtered through 25 mm Gelman A/E glass fiber filters directly into 4-mℓ sample bottles with teflon-lined caps and immediately stored at 4° C for subsequent analysis. The rate studies were run until the dissolved oxygen concentration was reduced to approximately 1.0 mg/ℓ. Biodegradation studies of the non-volatile compounds were conducted in a similar manner except the 2.6ℓ CMB reactor was continuously aerated with compressed air to maintain dissolved oxygen levels in the 3 to 5 mg/ℓ range.

The second type of biodegradation rate study was conducted in the 10-liter experimental bioreactors operated with aeration. The units were temporarily converted from continuous-flow to batch modes by stopping the influent flows to and sludge waste flows from the reactors. The bioreactors were spiked with 20-μℓ of methanol solution containing the toxic organic compound to which the particular units had been acclimated, producing initial concentrations of 30 to 60 μg/ℓ. Aeration rates used during the CMB biodegradation studies were the same as those used when the bioreactors were operated in continuous flow modes and ranged from 3.8 to 4.2 ℓ/min. Reductions in the aqueous concentrations of the toxic organic compounds were a result of both air stripping and biodegradation.

5.4.4. Carbon Absorption Rate Studies

Completely-mixed batch studies were conducted to evaluate the rate of adsorption of selected toxics by powdered activated carbon. Adsorption rate studies were conducted in 2.6 and 3.0 liter glass reactors mixed with paddle stirrers. Adsorption experiments were begun by filling the appropriate reactor with a desired background solution and spiking the contents with 10 to 50 μℓ of a methanol solution containing one of the toxic compounds. Samples to measure the initial concentration were taken after the contents were well-mixed. A known weight of powdered carbon in a slurried form was added to the reaction vessel and samples were taken at specified time intervals. The powdered carbon was slurried approximately 20 to 30 minutes prior to being added to the batch reactor to ensure complete wetting of the carbon surface. Samples were withdrawn with a 20-μℓ glass syringe and either filtered or centrifuged immediately to remove the powdered carbon.

5.5 COMPLETELY-MIXED BATCH EQUILIBRIUM STUDIES

5.5.1. Carbon Adsorption Isotherms

5.5.1.1. Toxic Organic Compounds

Equilibrium adsorption isotherms were conducted to quantify the adsorption characteristics of each compound with various powdered activated carbons in background solutions which included deionized-distilled water, reactor effluent, and synthetic wastewater. All isotherms were performed by a bottle point technique employing 150-mℓ Hypo-vials® sealed with teflon-lined aluminum caps. Known amounts of PAC in a slurried form were pipetted from a concentrated slurry to each bottle, and the bottle was filled with the appropriate background solution. The maximum volume of slurried PAC transferred was 10 mℓ to minimize dilution of the background solution. Each bottle was spiked with 10 to 20 μℓ of a methanol solution containing one of the toxic organics, sealed, and mixed until equilibrium conditions were achieved.

The type of mixing used depended upon the volatility of the compound. Isotherms for the most volatile compounds, benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene, were conducted in Hypo-vials® without headspace. Mixing for these studies was accomplished with small teflon-coated magnetic stirring bars. The bottles were stirred with a gang-mixer at speeds sufficient to maintain well-mixed conditions. Care was taken to prevent heat from the stirrer from changing the temperature in the isotherm bottles. Isotherms with 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, nitrobenzene, and lindane were conducted in bottles filled to a total volume of 100 mℓs. Mixing was accomplished with a reciprocal shaker.

Isotherm bottles containing benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene were filtered to remove the powdered carbon. Samples were withdrawn with a 20 mℓ syringe and filtered with an in-line filter apparatus containing a 25 mm Gelman A/E glass-fiber filter. Background studies showed no significant adsorption of the five volatile compounds on either the filter apparatus or filter paper. The filtrates were collected in 8-mℓ sample bottles filled without a headspace, sealed with teflon-lined caps, and stored at 4° C for subsequent analysis by the purge and trap procedure outlined in Section 6.

Samples from isotherm bottles containing 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, nitrobenzene, and lindane were transferred into 15-mℓ test tubes with teflon-lined screw caps and centrifuged at approximately 2000 rpm for 15 minutes. Aliquots of the supernatant were pipetted into 6-dram vials containing a known volume of hexane. The vials were capped with teflon-lined lids and agitated on a reciprocal shaker to facilitate partitioning of the toxic organic into the hexane. Extraction vials were stored inverted at 4°C for subsequent analysis by a gas chromatograph equipped with a ^{63}Ni electron capture detector.

5.5.1.2. TOC Isotherms

Equilibrium isotherms were conducted to quantify the adsorption of wastewater soluble TOC by the powdered activated carbons. Isotherms were conducted in 150-mℓ hypo-vials® by adding known weights of dry carbon and 100 mℓs of the appropriate wastewater solution. Mixing was accomplished with a magnetic stirrer. After equilibrium conditions were reached a sample from each bottle was filtered through a 25 mm Gelman A/E glass-fiber filter and acidified with two drops of concentrated phosphoric acid. Analyses for TOC were conducted with a Dohrman low level Total Organic Carbon Analyzer, Model DC80.

5.5.2. Biological Sorption Studies

Biological sorption studies were performed to evaluate the partitioning of the three most hydrophobic organics 1,2-dichlorobenzene, lindane and 1,2,4-trichlorobenzene, between the aqueous and biological solid phases. The experiments were conducted with activated sludge of a known suspended solids concentration from an activated sludge bioreactor not receiving any of toxic organic compounds in the influent. Activated sludge was transferred to a two-liter graduated cylinder and gravity settled to concentrate the biological solids. A standard suspended solids procedure was used to measure the concentration of the settled sludge. Various volumes of the concentrated biological solids were added to 150-mℓ Hypo-vials® and diluted to 150 mℓs with distilled water to eliminate headspace and minimize volatilization. Each vial was spiked with 10 μℓ of a methanol solution containing a toxic organic compound, sealed, and mixed with a magnetic stirrer for three hours. Samples from each vial were centrifuged and the supernatant was extracted with hexane. All extracts were agitated for fifteen minutes and stored at 4° C for subsequent analysis. Uncentrifuged samples containing biological solids were also extracted to complete a mass balance on the compound and determine if any biodegradation had occurred.

SECTION 6

ANALYTICAL METHODOLOGIES

Considerable energy was devoted to developing the analytical methodologies necessary to measure microgram-per-liter concentrations of the toxic organic compounds in bioreactor influents and effluents and nanogram-per-liter concentrations in the bioreactor off-gases. The ability to measure influent, effluent, and off-gas concentrations in an efficient, reproducible manner was essential for completing mass balances for each toxic organic compound. A summary of the analytical procedures developed for aqueous and off-gas analyses of the toxic compounds is presented in this section.

6.1 AQUEOUS SAMPLES

Two gas chromatographic techniques were used to measure the individual compounds in aqueous samples: purge and trap and liquid/liquid extraction. A summary of the analytical methods used in the aqueous analyses of each compound is given in Table 6-1.

6.1.2 Purge and Trap

A purge and trap procedure was used to analyze the volatile compounds benzene, toluene, ethylbenzene, o-xylene, 1,2-dichlorobenzene and 1,2,4,-trichlorobenzene. It represents an extension of the static headspace analysis to a dynamic system in which volatile organics are continuously purged from the aqueous phase by an inert gas and collected on a short chromatographic column.

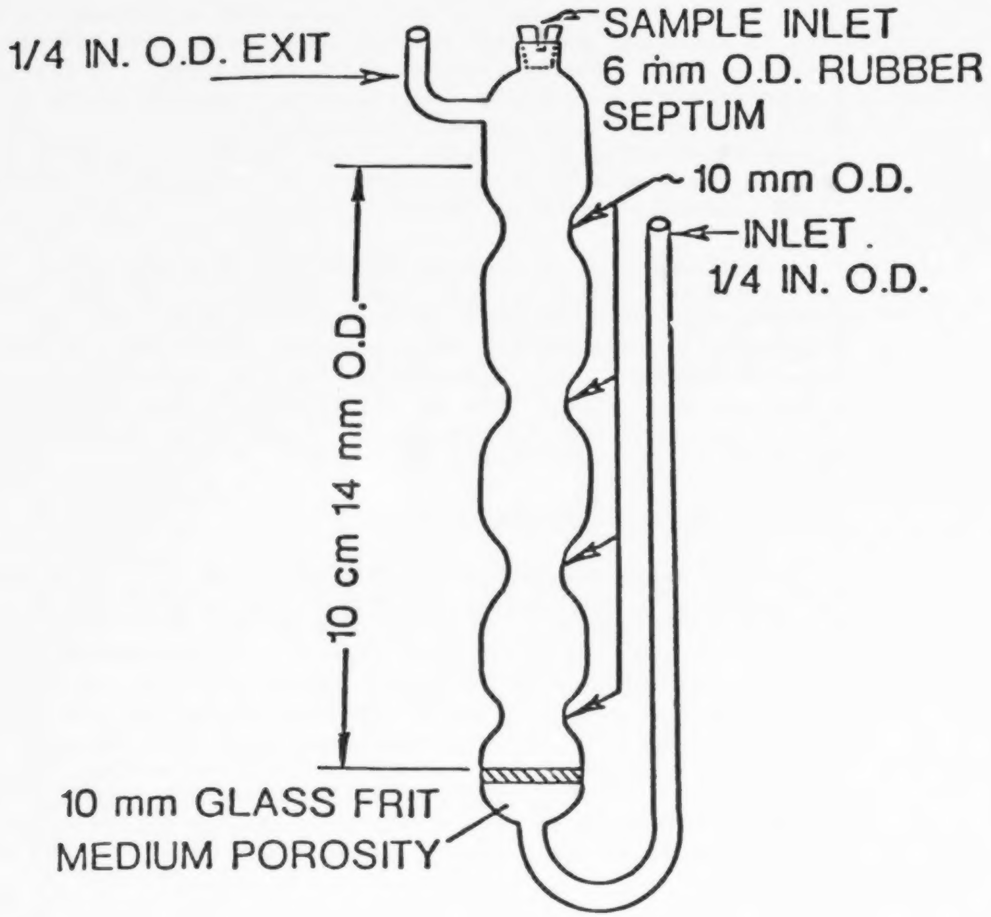
The purge and trap procedure used in the volatile organics analyses represents a modification of various methods reported to give reproducible results at low microgram-per-liter concentrations (45,46). A 1-to 5-ml aliquot of aqueous sample was added to the purging device shown in Figure 6 and purged for 15 minutes at room temperature with $N_2(g)$ at a flow rate of 50 ml/min. The purging temperature was increased to 55° by placing the purging device in a water bath for aqueous samples containing 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. Volatilized organics were continuously collected on a 6 in x 4 mm ID glass trap packed with Tenax GC and attached to the exit tube on the purging device shown in Figure 6-1. Glass wool plugs were placed in each end such that the trap contained approximately 5 inches of adsorbent.

TABLE 6-1

ANALYTICAL METHODS USED FOR AQUEOUS SAMPLES

Compound	Procedure	Detector	Limit of Detection (μg/ℓ)*
Benzene	Purge/Trap	FID	0.2
Toluene	Purge/Trap	FID	0.2
Ethylbenzene	Purge/Trap	FID	0.2
o-Xylene	Purge/Trap	FID	0.4
Chlorobenzene	Purge/Trap	FID	0.4
1,2-Dichlorobenzene	Purge/Trap Liquid/Liquid Extraction	FID EC(Ni^{63})	1.0 0.1
1,2,4-Trichlorobenzene	Purge/Trap Liquid/Liquid Extraction	FID EC(Ni^{63})	1.0 0.1
Nitrobenzene	Liquid/Liquid Extraction	EC(Ni^{63})	0.1
Lindane	Liquid/Liquid Extraction	EC(Ni^{63})	0.1

*Based upon: 10 ml sample size for Purge and Trap
10-fold concentration during extraction procedure



1/4 IN. O.D. EXIT
SAMPLE INLET
6 mm O.D. RUBBER
SEPTUM
10 mm O.D.
INLET.
1/4 IN. O.D.
10 cm 14 mm O.D.
10 mm GLASS FRIT
MEDIUM POROSITY

FIGURE 6-1

Purging device used for sampling volatile organic compounds.

The collected organics were measured by attaching the sampling trap to the modified injection port of a Varian 2740 gas-chromatograph (GC). An $N_2(g)$ carrier flow was introduced through the trap while it was heated at 250°C to transfer the collected organics to the front end of a gas chromatographic column maintained at 20°C in the GC oven. A temperature program was used to heat the chromatographic column from 20°C to 140°C at 20°C/min to separate the compounds for detection by a flame ionization detector (FID).

Two different gas chromatographic columns were used. One column, 2 ft x 1/8 in stainless steel packed with 0.2% Carbowax 1500 on Carbopack C, effected good separation of benzene, toluene, ethylbenzene, o-xylene and chlorobenzene. The second column, used for o-dichlorobenzene and 1,2,4-trichlorobenzene, was 6 ft x 1/8 in stainless steel packed with 10% OV-17 on 60/80 Gas Chrom Q. A summary of the pertinent operating conditions used in the purge and trap procedure is given in Tables 6-2 and 6-3.

6.1.2 Liquid/Liquid Extraction

Liquid/liquid extraction takes advantage of the preferential partitioning of hydrophobic organics into an organic solvent from an aqueous sample when the two phases are mixed. This procedure was used in the analysis of nitrobenzene, lindane, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. Extractions were performed by adding an aliquot of sample to a 25-ml Teflon-lined screw top vial containing 2 to 4 ml of hexane. The vials were agitated using a reciprocal shaker to effect partitioning of the toxic organic compounds into the hexane solvent. Samples were analyzed with a Hewlett-Packard 5880 gas chromatograph equipped with an electron capture (Ni^{63}) detector. A 6 ft x 1/8 in glass chromatographic column packed with 3% 60/80 Gas Chrom Q was used.

6.2. OFF-GAS SAMPLES

The volatile nature of most of the compounds used in this study necessitated the development of a sensitive, reproducible method for measuring the concentration of each compound in the bioreactor off-gases. The procedure used in this study was an adaptation of various methods developed for sampling air pollutants (45-48), all of which are essentially an extension of the purge and trap procedure previously explained.

Approximately one hour prior to sampling the reactor, the off-gas sampling valve located in the reactor lid was closed. The off-gases were then forced through the effluent drainage line and discharged approximately two feet under water in a constant depth discharge reservoir creating a slight positive pressure in the reactor. An off-gas sample was collected by connecting a sampling trap to a closed off-gas sampling valve on the reactor lid. Sampling traps used for off-gas analyses were identical to those used in the purge and trap procedure. Off-gas samples were collected by opening the sampling valve

TABLE 6-2

SUMMARY OF PERTINENT OPERATING CONDITIONS USED IN THE PURGE AND TRAP ANALYSIS OF BENZENE, TOLUENE, ETHYLBENZENE, O-XYLENE AND CHLOROBENZENE

PURGING SEQUENCE

Time	15 min
Purge Gas	Nitrogen
Flow Rate	50 mℓ/min
Temperature	20°C
Trap	5" x 4 mm ID glass packed with Tenax GC

DESORPTION SEQUENCE

Time	4 min
Temperature	250°C
Carrier/Flow	N_2(g) at 40 mℓ/min

GAS CHROMATOGRAPHY OPERATING CONDITION

Temperature Program Sequence	
initial oven temp.	20°C
final oven temp.	140°C
temp. program rate	20°C/min
Carrier/Flow	N_2(g) at 40 mℓ/min
Column	2' x 1/8" stainless steel packed with 0.1% Carbowax 1500 on Carbopack C
Detector	FID air flow 300 mℓ/min hydrogen flow 30 mℓ/min

TABLE 6-3

SUMMARY OF PERTINENT OPERATING CONDITIONS USED IN THE PURGE AND TRAP ANALYSIS OF 1,2-DICHLOROBENZENE AND 1,2,4-TRICHLOROBENZENE

PURGING SEQUENCE

Time	15 min
Purge Gas/Flow	Nitrogen/50 mℓ/min
Temperature	55°C
Trap	5" x 4 mm ID glass packed with Tenax GC

DESORPTION SEQUENCE

Time	5 min
Temperature	250°C
Carrier/Flow	N_2(g) at 40 mℓ/min

GAS CHROMATOGRAPHY OPERATING CONDITION

Temperature Program Sequence

initial oven temp.	20°C
final oven temp.	140°C
temp. program rate	20°C/min

Carrier/Flow	N_2(g) at 40 mℓ/min
Column	6' x 1/8" stainless steel packed with 10% OV-17 on 60/80 Gas Chrom Q
Detector	FID air flow 300 mℓ/min hydrogen flow 30 mℓ/min

and allowing a portion of the off-gas to pass through the sampling trap and a calibrated air flow meter for 4 to 10 minutes at flow rates ranging from 60 to 80 ml/min. The procedure used to analyze the volatilized organics collected on the sampling trap was identical to the one described for the purge and trap procedure. The small flow of the off-gas diverted through the sampling trap (approximately 2% of the total off-gas flow) was insufficient to alter the steady state conditions inside the bioreactor.

SECTION 7

RESULTS: VOLATILIZATION STUDIES

7.1 EFFECT OF AIR-STRIPPING ON FATE OF TOXIC ORGANICS IN BIOREACTORS WITHOUT ACTIVATED SLUDGE

Activated sludge treatment systems typically employ diffused or mechanical aerators to supply oxygen to the bacteria and to maintain sufficient mixing to keep the biomass in suspension. Such mixing and aeration can effect purging of volatile compounds from wastewaters. A significant number of the 114 organic priority pollutants can be characterized as volatile compounds, suggesting that air stripping could be a significant factor affecting the fate of these compounds during treatment. Five of the toxic compounds used in this study can be classified as purgeable organics; benzene, toluene, chlorobenzene, ethylbenzene and o-xylene, and two more, o-dichlorobenzene and 1,2,4-trichlorobenzene are considered volatile.

Initial studies conducted with the 10-liter bioreactors operated in continuous flow modes without activated sludge and with influents of synthetic wastewater spiked with a toxic organic compound identified the importance of air stripping. The summary of representative influent, effluent and off-gas values for each compound given in Table 7-1 shows that air stripping effected a 90 to 96% reduction in the aqueous concentrations of all of the compounds except nitrobenzene and lindane. The mean hydraulic residence time and aeration rate used in the baseline air stripping studies were 5.5 hours and 4.0 ℓ/min, respectively.

7.2 DETERMINATION OF VOLATILIZATION RATE COEFFICIENTS

The transfer of a volatile compound from a dilute aqueous phase to a gaseous phase can be represented by the first-order expression

$$-\frac{dC}{dt} = k_v C \qquad (7\text{-}1)$$

where C (μg/ℓ) is the aqueous concentration, t (min) is time and k_v (min^{-1}) is the first order volatilization rate coefficient. Air

TABLE 7-1

EFFECT OF AIR STRIPPING ON REMOVALS OF TOXIC ORGANIC COMPOUNDS FROM BIOREACTORS WITHOUT ACTIVATED SLUDGE

	Influent (μg/ℓ)	Effluent (μg/ℓ)	Effluent (% of Inf.)	Off Gas ng/ℓ	Off Gas (% of Inf.)
Benzene	108.4	3.6	3.3	835	96.7
Toluene	114.8	4.2	3.7	829	96.3
Ethylbenzene	95.1	2.8	2.9	765	97.1
o-Xylene	105.1	4.0	3.8	838	96.2
Chlorobenzene	100.6	3.5	3.5	805	96.5
o-Dichlorobenzene	98.5	9.5	9.6	648	90.4
1,2,4-Trichlorobenzene	104.2	10.0	9.6	674	90.4
Nitrobenzene	95.0	71.3	75.0	188	25.0
Lindane	100.0	100.0	100.0	0	0

stripping studies were conducted in the 10-liter bioreactors operated in batch modes at 20°C without activated sludge to evaluate volatilization rate coefficients for benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, o-dichlorobenzene, and 1,2,4-trichlorobenzene. The bioreactors were spiked with 10μℓ of a methanol solution containing one or more toxic compounds and mixed for five minutes to produce initial concentrations ranging from 70 to 100 μg/ℓ. Air flows were then begun, and samples were withdrawn at four to five minute intervals from a sampling port on the side of each reactor. The volatilization of a single toxic compound was not affected by the presence of additional toxic compounds at the low concentrations studied. Typically, volatilization studies were conducted with two or more toxic organic compounds.

Results for each toxic organic compound from stripping studies conducted under identical conditions have been plotted in Figure 7-1. Initial concentrations for the results in Figure 7-1 ranged from 70 to 85 μg/ℓ. There was no removal of lindane and only a small reduction in the concentration of nitrobenzene after 60 minutes, therefore no further attempts were made to quantify the stripping of lindane and nitrobenzene. Significant removals of the other compounds occurred and the following relative order of volatilization was observed:

> ethylbenzene > toluene ≈ benzene > o-xylene > chlorobenzene >
> 1,2-dichlorobenzene ≈ 1,2,4-trichlorobenzene

Volatilization rate coefficients, k_v, were obtained from the slope of the least-squares linear regression line for data plotted as the natural logarithm of concentration, ln C, versus time as shown in Figure 7-2 for an aeration rate of 4.0 ℓ/min. The volatilization rate coefficients from air-stripping studies conducted at 4.0 ℓ/min are summarized in Table 7-2. The last column in Table 7-2, k_v(solute)/k_v(benzene), compares the volatility of each compound to that of benzene.

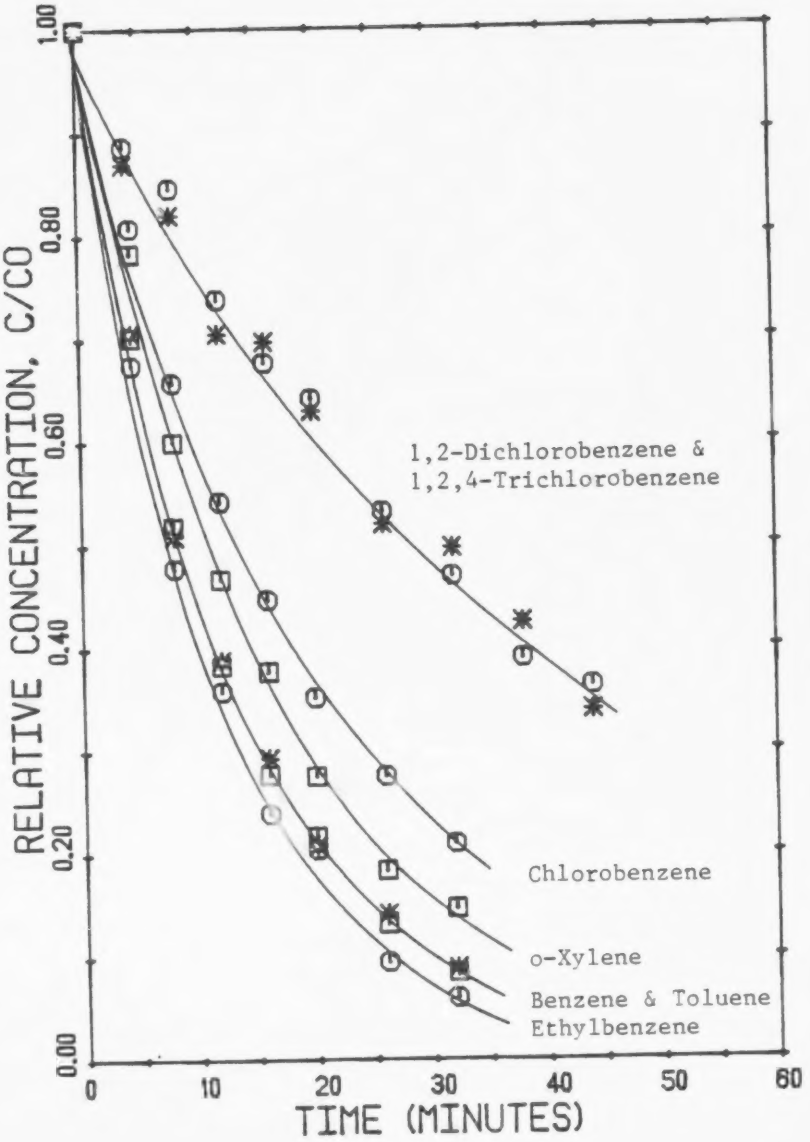


FIGURE 7-1. Volatilization of selected toxic organic compounds from 10-liter bioreactors without activated sludge. (Aeration rate = 4.0 liters/min.)

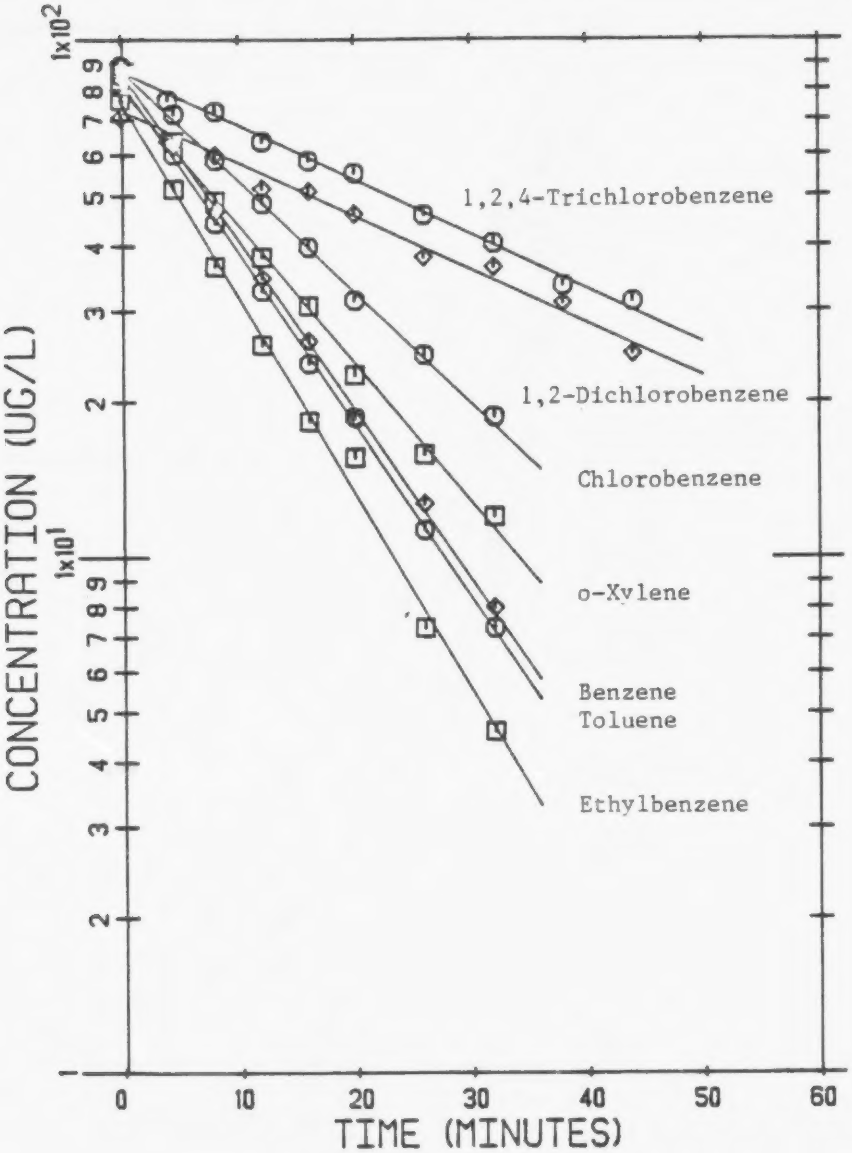


FIGURE 7-2. Data points and best-fit lines describing the volatilization rates of selected toxic organic compounds from 10-liter bioreactors without activated sludge and with air-tight lids. (Aeration rates = 4.0 liters/min.)

TABLE 7-2

VOLATILIZATION RATE COEFFICIENTS FROM AIR-STRIPPING STUDIES CONDUCTED IN THE 10-LITER BIOREACTORS WITH AN AERATION RATE OF 4.0 1/min

Compound	$k_v(\text{min}^{-1})$	corr.	$k_v(\text{solute})/k_v(\text{benzene})$
Ethylbenzene	0.0874	0.997	1.16
Toluene	0.0765	1.000	1.02
Benzene	0.0754	1.000	1.00
o-Xylene	0.0615	0.999	0.82
Chlorobenzene	0.0493	0.999	0.65
1,2-Dichlorobenzene	0.0240	0.997	0.32
1,2,4-Trichlorobenzene	0.0236	0.991	0.31

7.3 EFFECT OF AERATION RATE ON THE VOLATILIZATION RATE COEFFICIENTS

The effect of the aeration rate, Q_a, upon the volatilization rate coefficients was determined by conducting stripping studies for each compound at aeration rates ranging from 1.0 to 5.0 1/min. Results from each of these studies, plotted as ln C versus time, are presented in Figures 7-3 through 7-9. The volatilization rate coefficients from each compound were observed to increase linearly with the aeration rate as shown by Figure 7-10. The relationship between k_v and Q_a can be described by the equation

$$k_v = k_{v,o} + Q_a L \qquad (7\text{-}2)$$

where $k_{v,o}$ (min^{-1}) is the calculated intercept and $L(1^{-1})$ is the slope of the line from a least-squares linear regression of the data, and Q_a (1/min) is the aeration rate. Values of L, $k_{v,o}$ and the correlation coefficient for each of the lines in Figure 7-10 are listed in Table 7-3.

Replicate studies conducted with benzene demonstrated that values of k_v were reproducible and not affected by different initial concentrations. Average values of k_v were used to calculate the volatilization parameters in Table 7-3 when replicate studies were run. Results from replicate benzene air stripping studies conducted at 4.0 1/min and presented in Figure 7-11 yielded volatilization rate coefficients of 0.0751 and 0.0755 min^{-1} for Run 1 and Run 2, respectively. The correlation coefficient was 0.999 in each case. Figure 7-12 shows results from benzene stripping studies with initial concentrations of 47 and 80 ug/1 and aeration rates of 3.0 1/min. Values of k_v were 0.0566 and 0.0573 min^{-1} for the runs with initial concentrations of 80 and 47 ug/1, respectively.

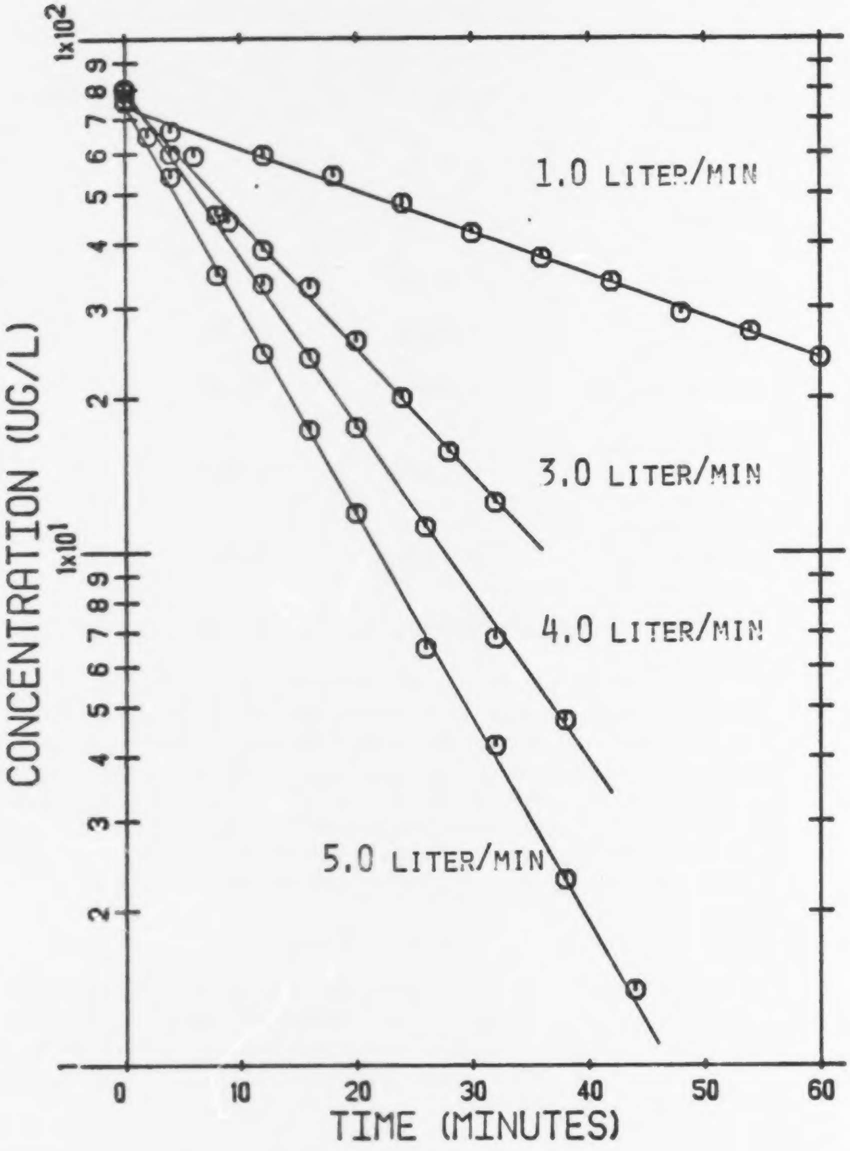


FIGURE 7-3. Effect of aeration rate on benzene volatilization rate from 10-liter bioreactors with air-tight lids and without activated sludge.

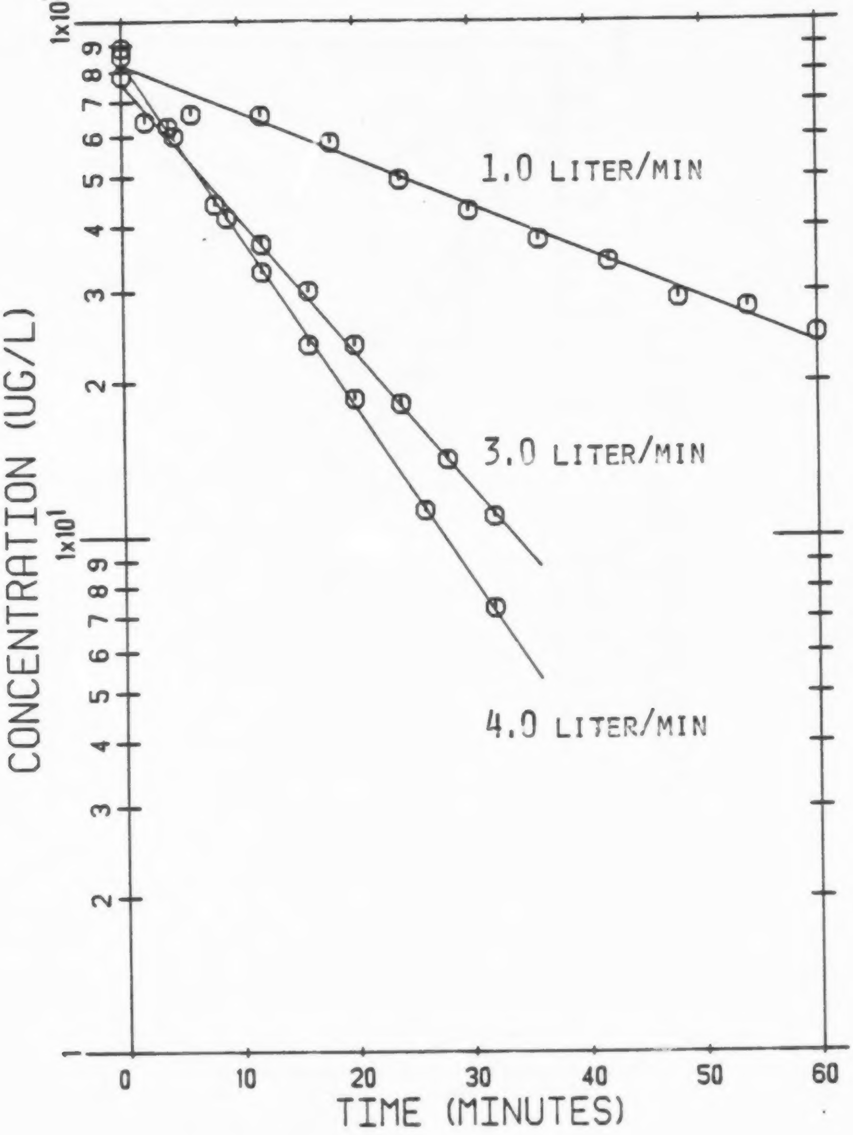


FIGURE 7-4. Effect of aeration rate on the toluene volatilization rate from 10-liter bioreactors with air-tight lids and without activated sludge.

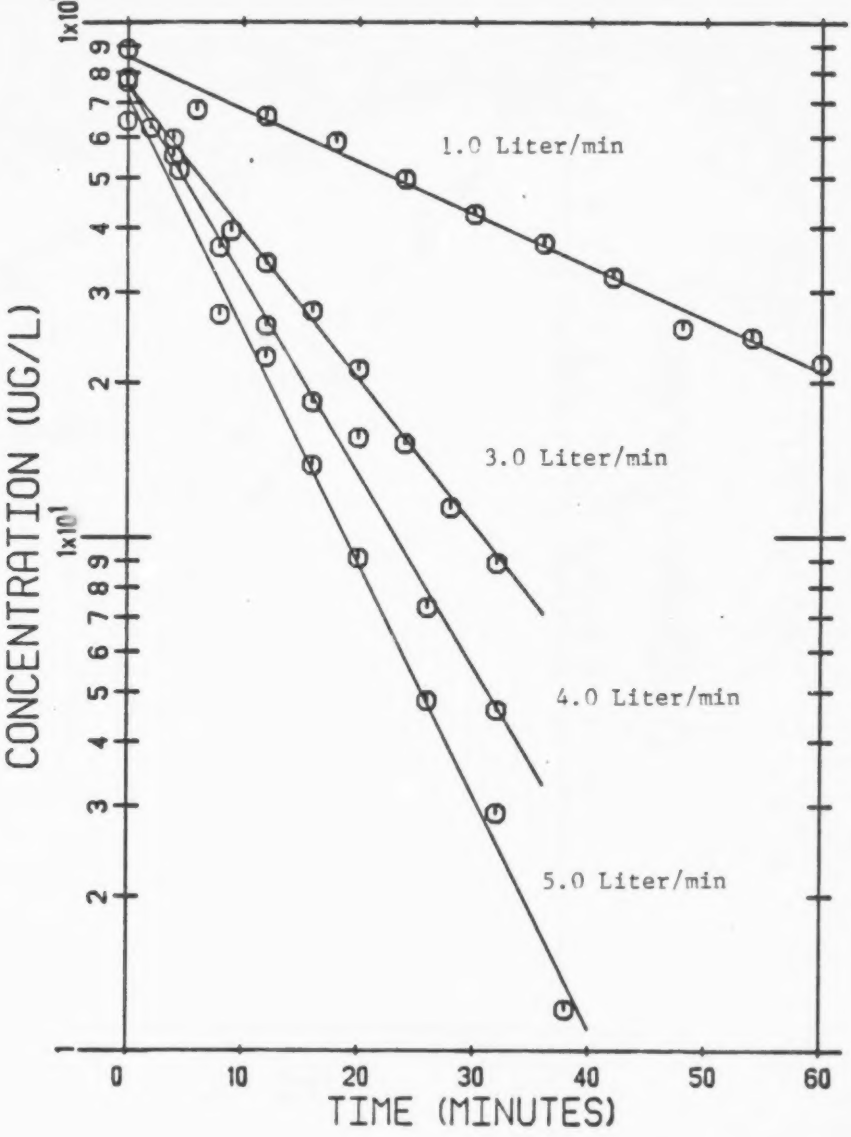


FIGURE 7-5. Effect of aeration rate on the ethylbenzene volatilization rate from 10-liter bioreactors with air-tight lids and without activated sludge.

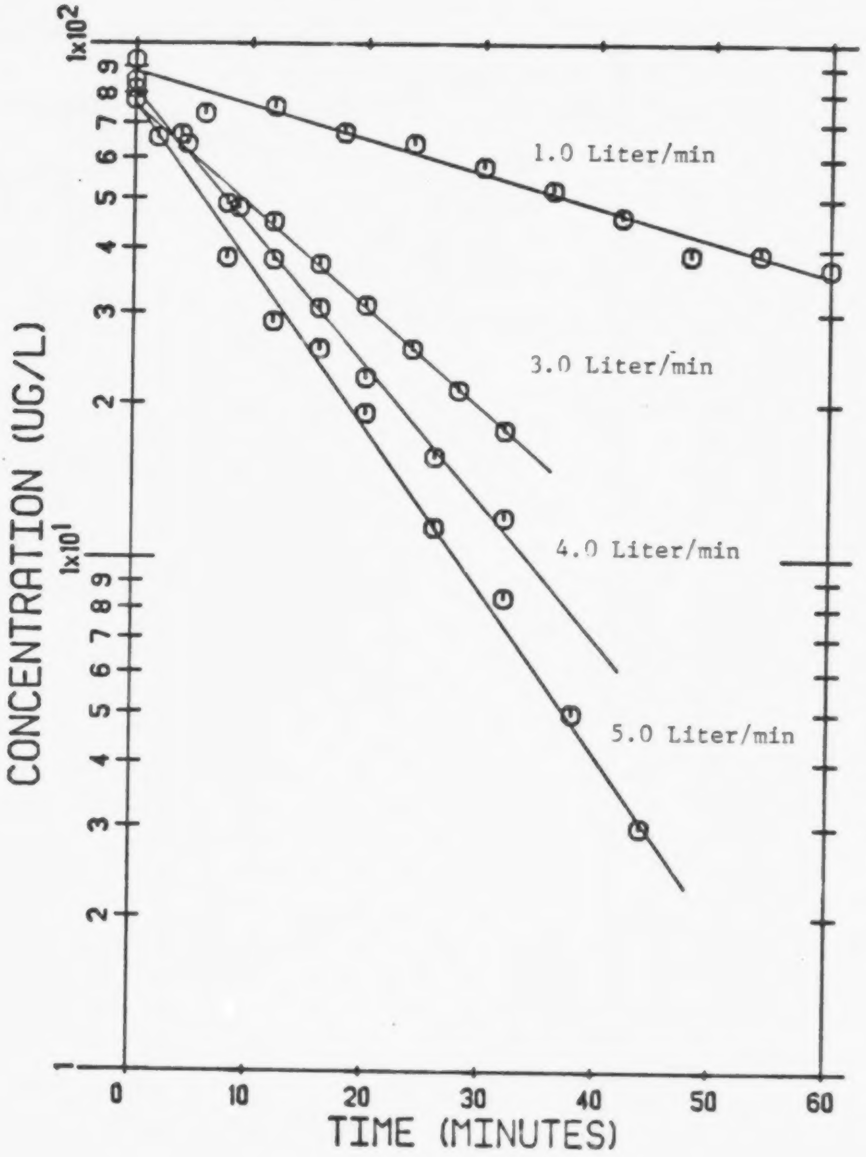


FIGURE 7-6. Effect of aeration rate on the o-xylene volatilization rate from 10-liter bioreactors with air-tight lids and without activated sludge.

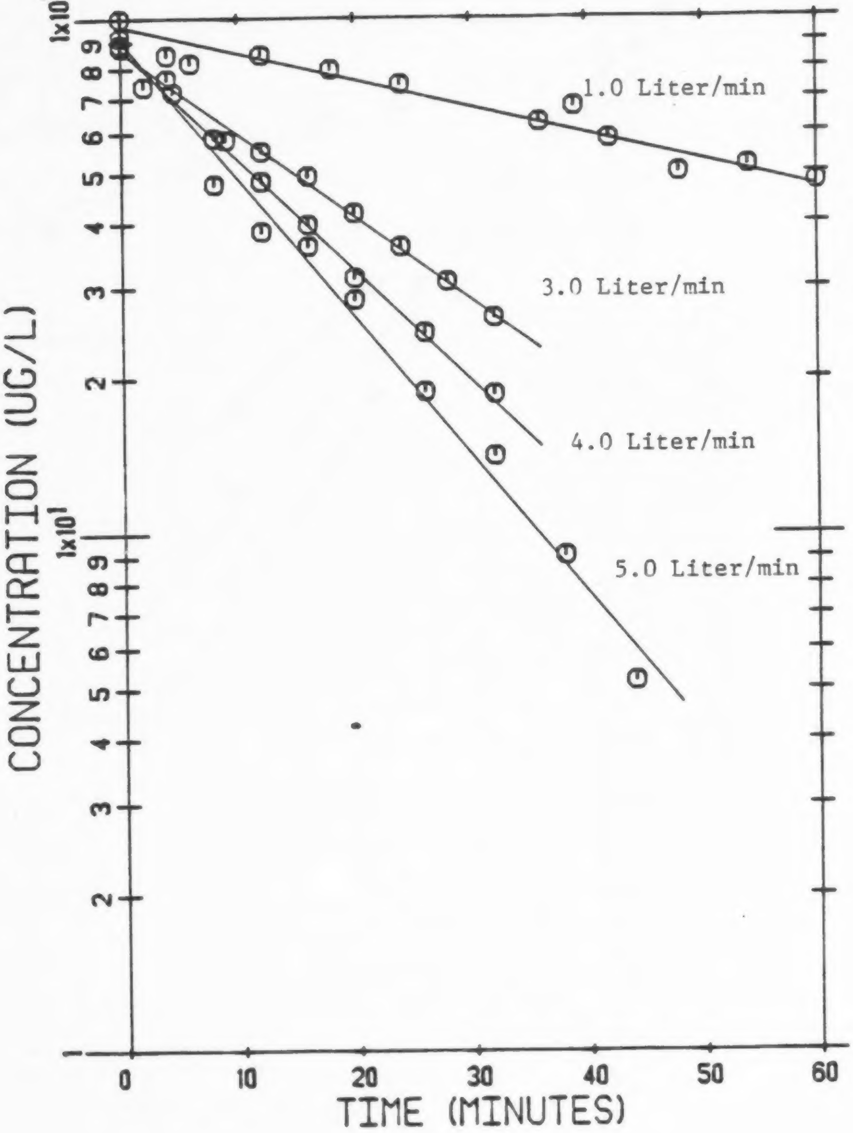


FIGURE 7-7. Effect of aeration rate on the chlorobenzene volatilization rate from 10-liter bioreactors with air-tight lids and without activated sludge.

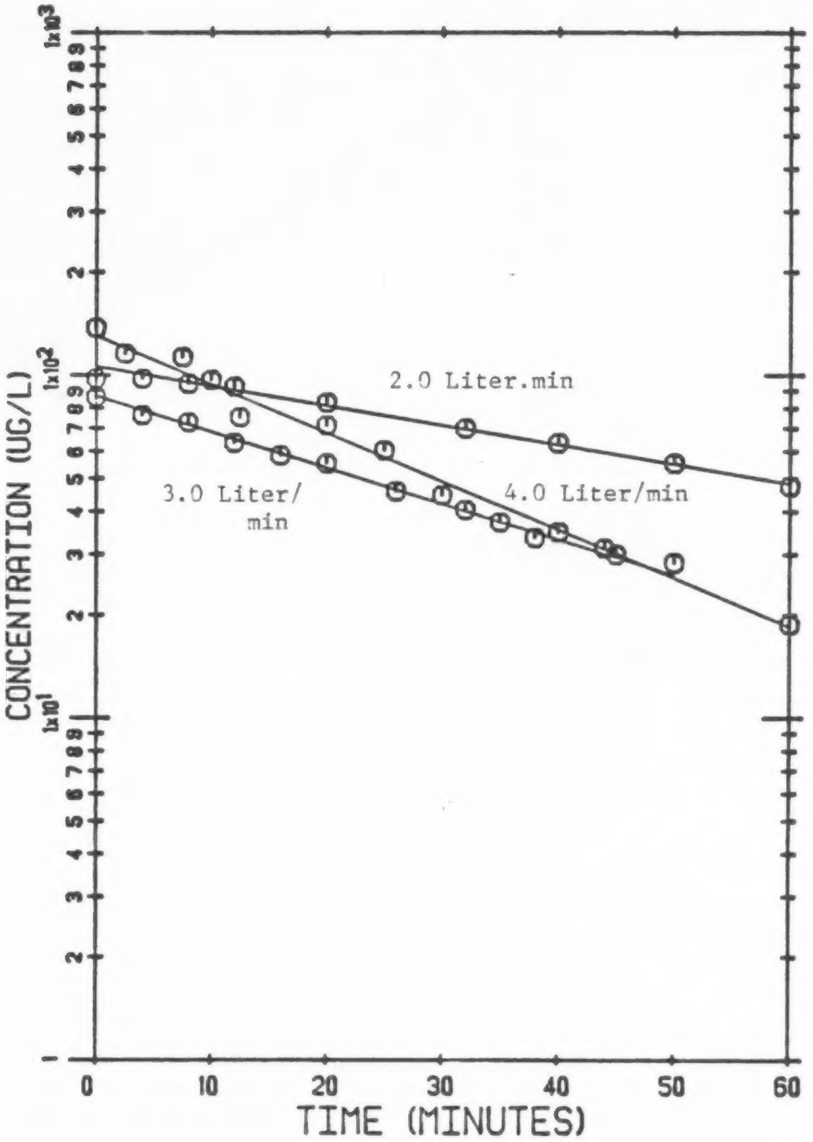


FIGURE 7-8. Effect of aeration rate on the 1,2-dichlorobenzene volatilization rate from 10-liter bioreactors with air-tight lids and without activated sludge.

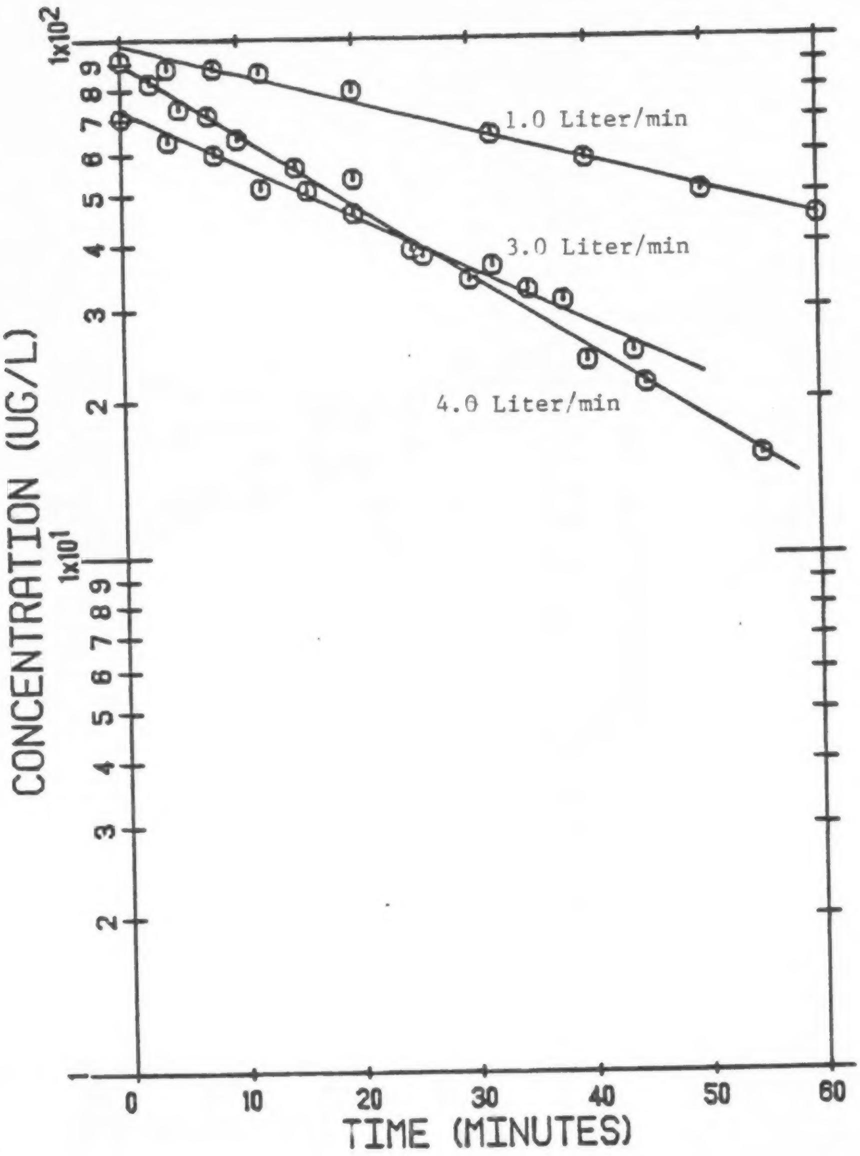


FIGURE 7-9. Effect of aeration rate on the 1,2,4-trichlorobenzene volatilization rate from 10-liter bioreactors with air-tight lids and without activated sludge.

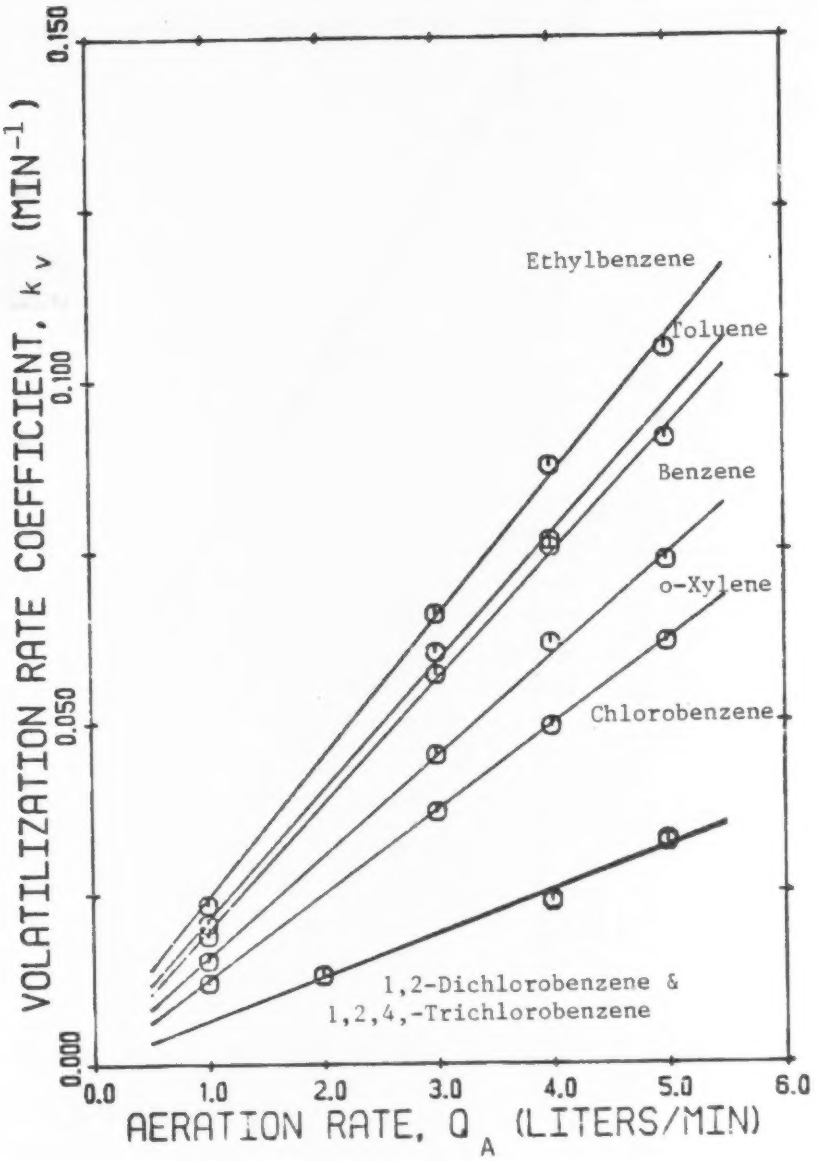


FIGURE 7-10. Effect of aeration rate on volatilization rate coefficients measured in 10-liter bioreactors with air-tight lids and without activated sludge.

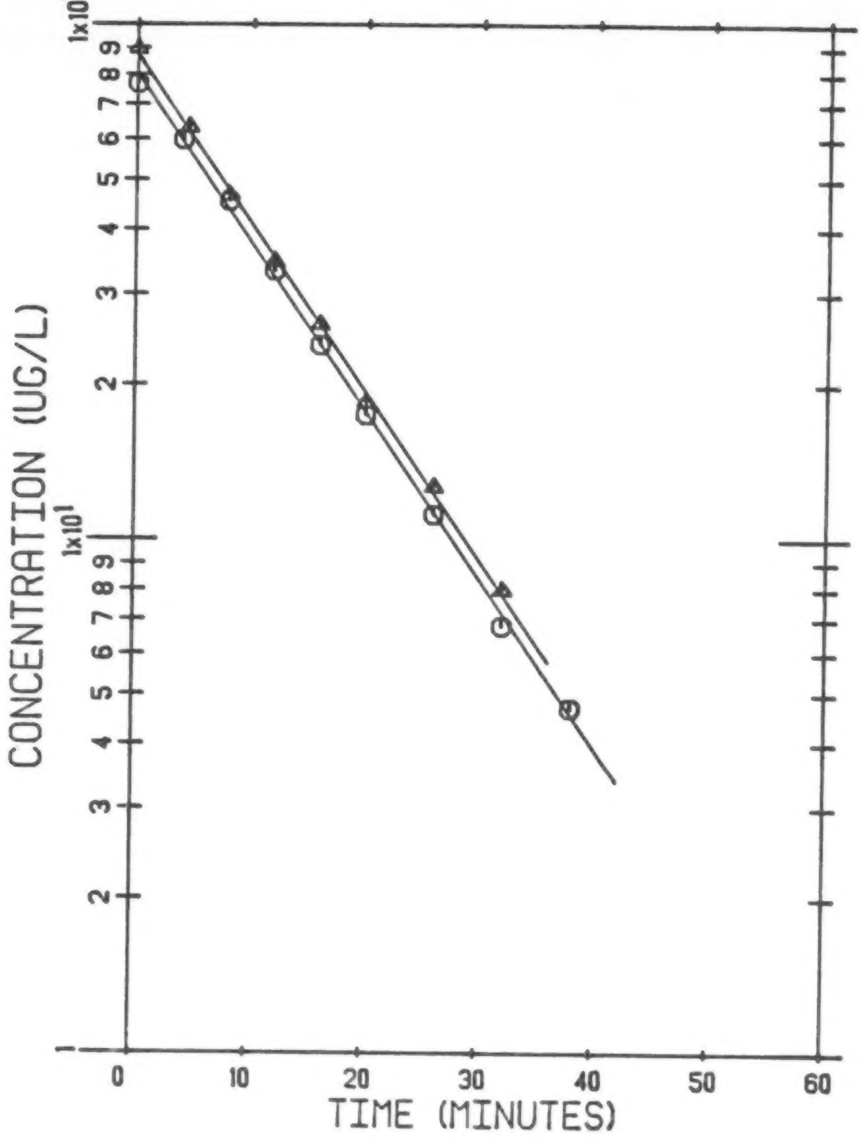


FIGURE 7-11. Data points and best-fit lines for results from replicate benzene volatilization studies in 10-liter sealed bioreactors with 4.0-liter/min aeration rates.

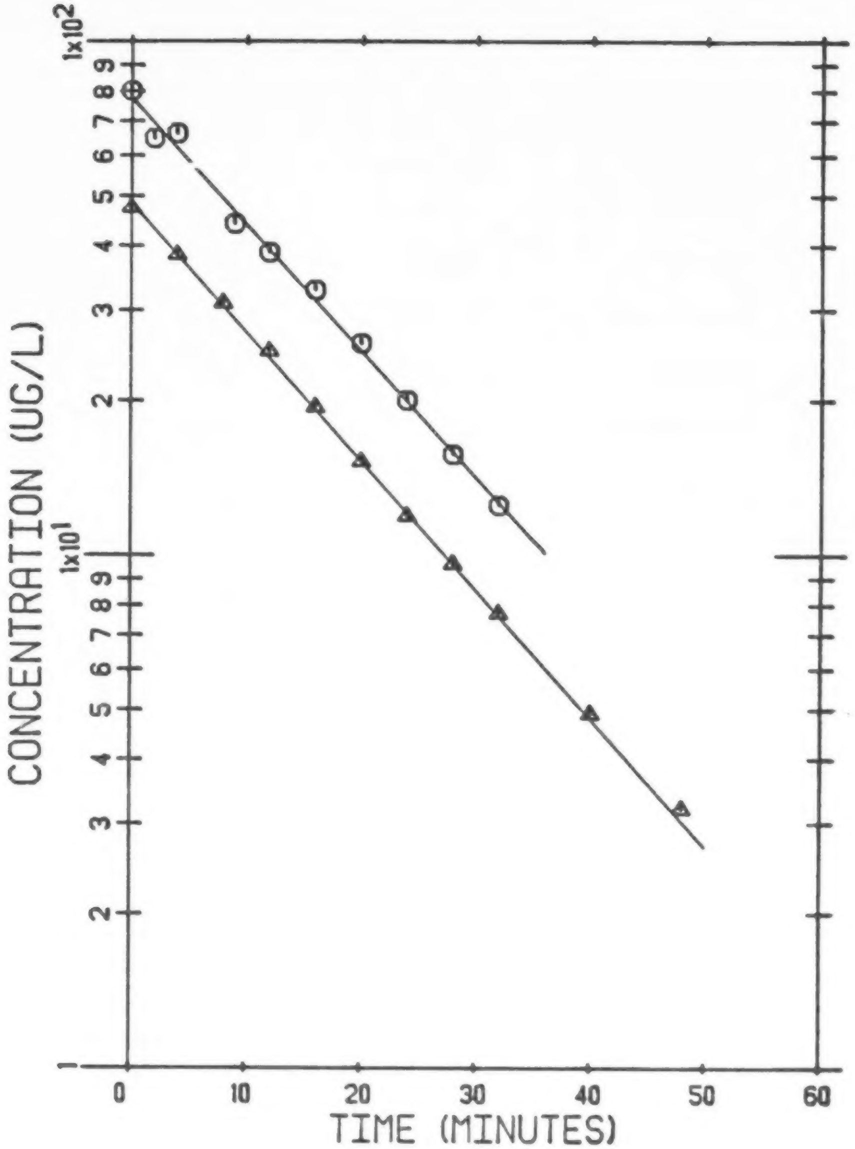


FIGURE 7-12. Data points and best-fit lines for results from replicate benzene volatilization studies in 10-liter sealed bioreactors with 3.0-liter/min aeration rates.

TABLE 7-3

VOLATILIZATION PARAMETERS RELATING k_v TO Q_a FOR AIR STRIPPING OF VOLATILE COMPOUNDS FROM 10-LITER BIOREACTORS WITH AIR-TIGHT LIDS

Compound	$k_{v,o}$ (min^{-1})	L(l^{-1})	Corr. Coef.
Benzene	0.0012	0.0183	0.999
Toluene	0.0023	0.0188	0.999
Ethylbenzene	0.0027	0.0205	0.999
o-Xylene	0	0.0148	0.999
Chlorobenzene	0	0.0124	1.000
1,2-Dichlorobenzene	0	0.0064	0.993
1,2,4-Trichlorobenzene	0	0.0063	0.992

7.4 AIR STRIPPING MODEL FOR CMF BIOREACTORS

Equation 7-2 was used to calculate k_v for any aeration rate used in the 10-liter bioreactors operated in continuous flow modes. Calculated values of k_v were incorporated into an air stripping model developed from a CMF reactor mass balance equation to predict both effluent and off-gas concentrations from bioreactors in which volatilization was the only mechanism effecting a reduction in aqueous concentration of an organic compound. The mass balance equation for the aqueous phase concentration is

$$V \frac{dC}{dt} = QC_i - QC_e - k_v C_e V \qquad (7-3)$$

Under conditions of steady-state the effluent concentration can be predicted by:

$$C_e = C_i/(1 + k_v\bar{t}) \qquad (7\text{-}4)$$

where C_e(μg/ℓ) is the effluent concentration, C_i (μg/ℓ) is the influent concentration, $\bar{t}$ (min) is the mean hydraulic retention time, V/Q_i, in the aeration section, V (ℓ) is the aqueous volume in the aeration section and Q_i(ℓ/min) is the aqueous flow rate. The mass balance equation on the gaseous phase, assuming toxic compounds are not present initially in the aeration gas, and that the gaseous phase is uniform in concentration overall, is

$$V_g \frac{dC_g}{dt} = -Q_gC_g + k_vC_eV \qquad (7\text{-}5)$$

where C_g (ng/ℓ) is the off-gas concentration, Q_g (ℓ/min) is the off-gas flow rate, and V_g(ℓ) is the volume of the gaseous phase. Under conditions of steady-state , the off-gas concentration can be predicted by

$$C_g = \frac{C_eVk_v}{Q_g} \qquad (7\text{-}6)$$

Substituting Equation 7-2 for the volatilization rate coefficient, k_v, in Equations 7-4 and 7-6 yields Equations 7-7 and 7-8 which were used to predict effluent and off-gas concentrations, respectively, from the 10-liter CMF bioreactors without activated sludges.

$$C_e = C_i/[1-\bar{t}(k_{v,o} + Q_aL)] \qquad (7\text{-}7)$$

$$C_g = \frac{C_e(V)}{Q_g}(k_{v,o} + Q_aL) \qquad (7\text{-}8)$$

Influents during the baseline stripping studies were composed of synthetic wastewater spiked with one or more toxic organic compounds. As compared in Table 7-4, the predicted effluent and off-gas values showed excellent agreement with measured values averaged from at least five bioreactor sampling periods. The bioreactors were operated with mean aeration rates and hydraulic retention times of 4.0 ℓ/min and 5.5 hours, respectively. Equation 7-8 was used to successfully predict off-gas concentrations from measured effluent concentrations in bioreactors with acclimated activated sludge.

TABLE 7-4

PREDICTED EFFLUENT AND OFF-GAS CONCENTRATIONS FROM BIOREACTORS WITHOUT ACTIVATED SLUDGE

Compound	Influent (μg/ℓ)	Measured Effluent (μg/ℓ)	Predicted Effluent (μg/ℓ)	Measured Off-Gas (ng/ℓ)	Predicted Off-Gas (ng/ℓ)
Benzene	120.3	4.6	4.5	846	835
Toluene	121.9	4.5	4.1	784	786
Ethylbenzene	112.0	3.5	3.7	758	787
o-Xylene	111.5	5.2	5.4	796	764
Chlorobenzene	130.9	6.8	6.7	790	828
1,2-Dichlorobenzene	105.2	10.8	11.0	691	706
1,2,4-Trichlorobenzene	117.7	12.2	12.2	765	772

7.5 EFFECT OF USING SEALED BIOREACTORS ON VOLATILIZATION RATE COEFFICIENTS

Off-gas sampling necessitated conducting all of the completely-mixed flow bioreactor studies in bioreactors sealed with air-tight lids. Such a reactor configuration is not representative of actual treatment facilities which utilize open reactors. The batch volatilization studies previously described were conducted in bioreactors equipped with air-tight lids to simulate the configuration of the experimental CMF units. An additional set of volatilization studies was conducted in open 10-liter bioreactors without air-tight lids to evaluate the effect of sealing the bioreactors with air-tight lids on air stripping.

Volatilization rate coefficients obtained from the open reactor stripping studies were greater than those obtained from the sealed reactor studies for a given aeration rate. Comparisons of results from volatilization rate studies conducted in open and sealed bioreactors at aeration rates of 4.0 ℓ/min are presented in Figures 7-13 through 7-17 for benzene, toluene, ethylbenzene, o-xylene and chlorobenzene, respectively. Volatilization rate coefficients for the five most volatile compounds measured in open and sealed bioreactors at aeration rates of 4.0 ℓ/min are given in Table 7-5. The ratio k_v(sealed)/k_v(open) for an aeration rate of 4.0 ℓ/min was similar for the five compounds and averaged 0.82.

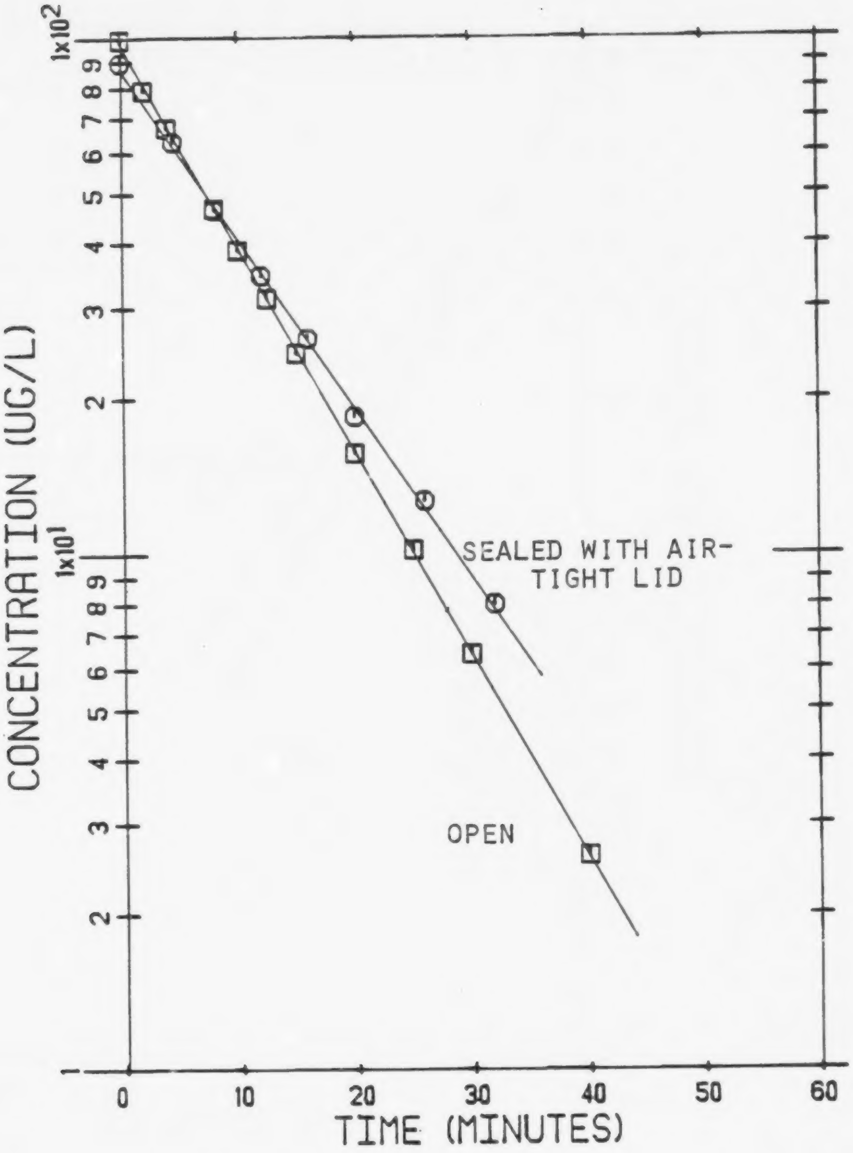


FIGURE 7-13. Benzene volatilization from sealed and open 10-liter bioreactors with 4.0 liter/min aeration rates.

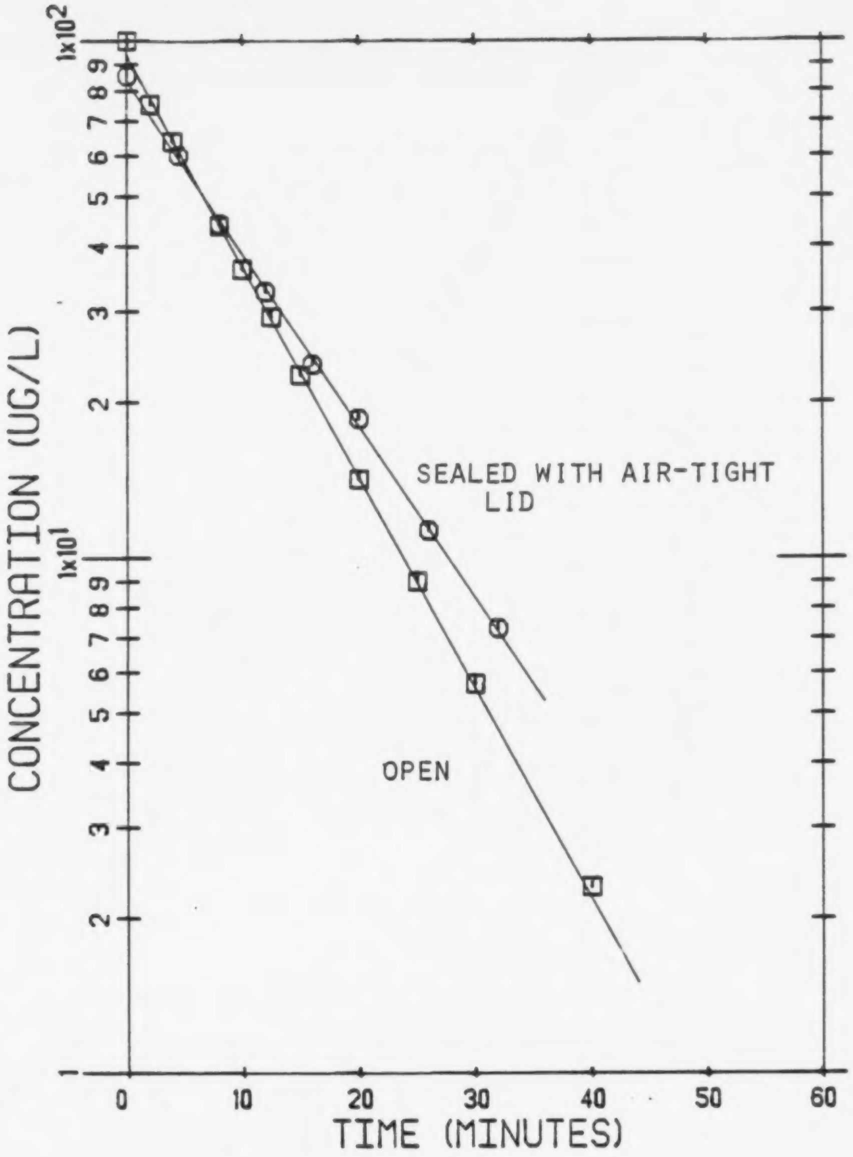


FIGURE 7-14. Toluene volatilization from sealed and open 10-liter bioreactors wich 4.0-liter/min aeration rates.

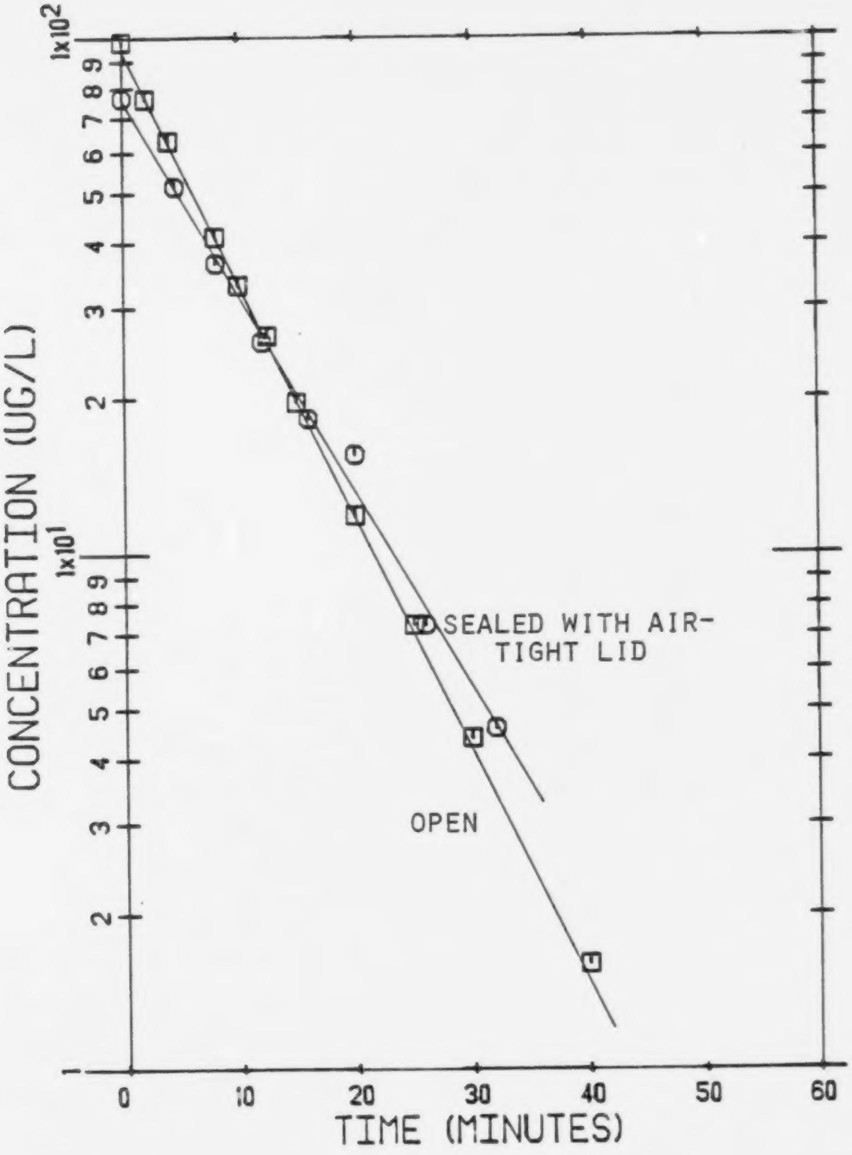


FIGURE 7-15. Ethylbenzene volatilization from sealed and open 10-liter bioreactors with 4.0-liter/min aeration rates.

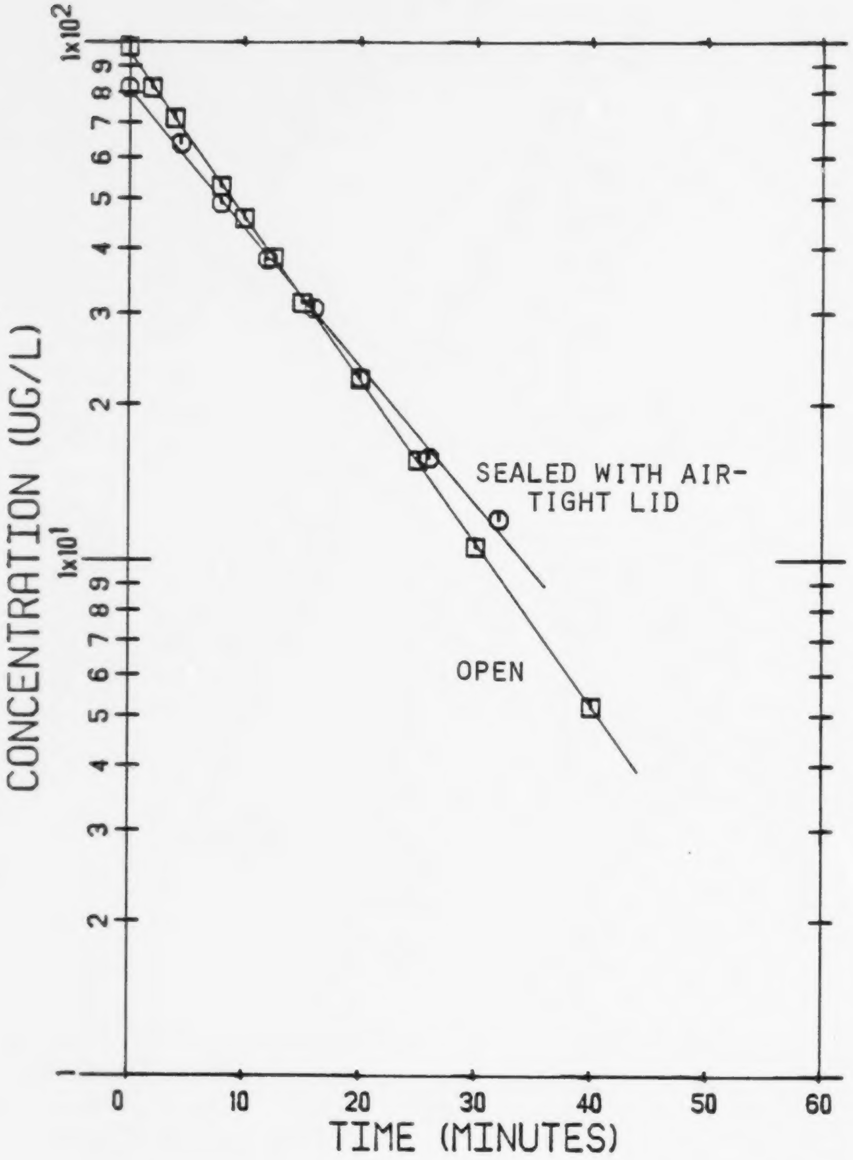


FIGURE 7-16. o-Xylene volatilization from sealed and open 10-liter bioreactors with 4.0-liter/min aeration rates.

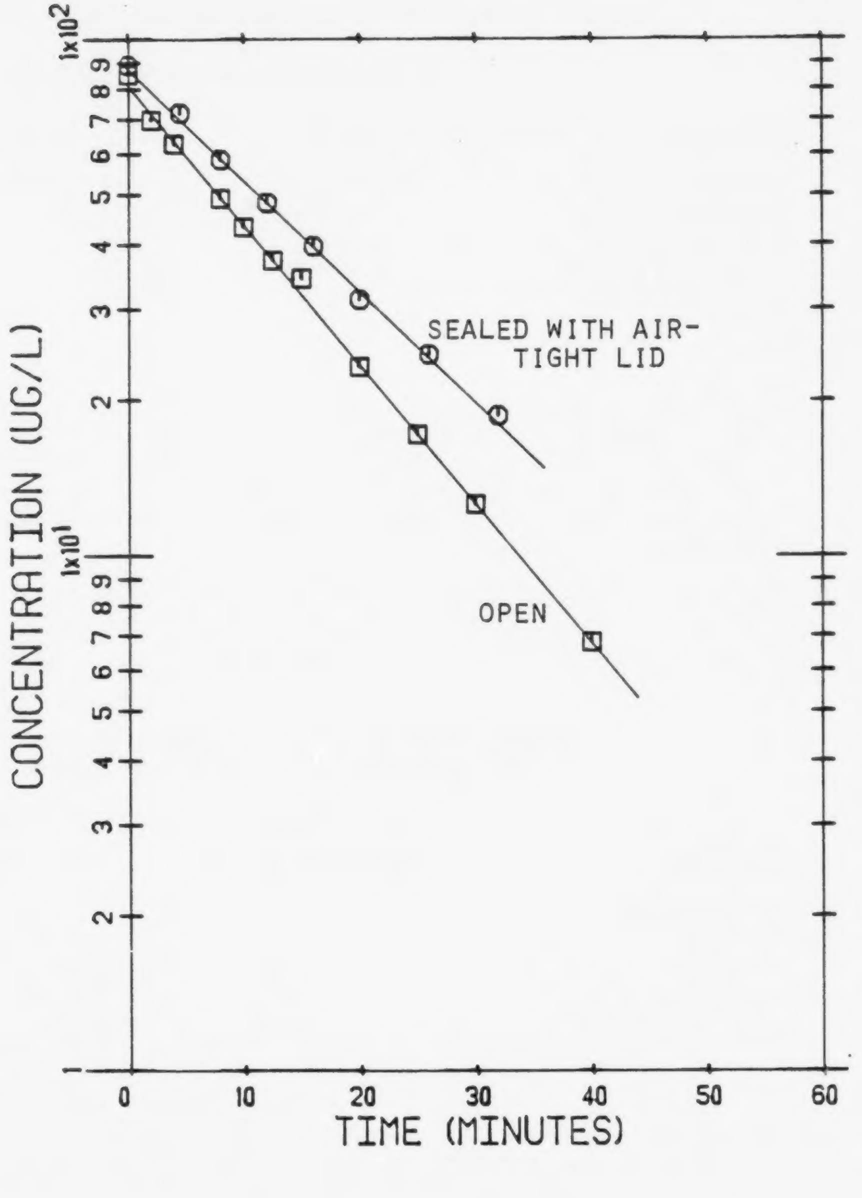


FIGURE 7-17. Chlorobenzene volatilization from sealed and open 10-liter bioreactors with 4.0-liter/min aeration rates.

TABLE 7-5

VOLATILIZATION RATE COEFFICIENTS IN OPEN AND SEALED BIOREACTORS AT AN AERATION RATE OF 4.0 ℓ/min

Compound	Volatilization Rate Coefficient, k_v (min^{-1}) Sealed	 Open	 k_v(sealed)/k_v(open)
Benzene	0.0754	0.091	0.83
Toluene	0.0765	0.093	0.82
Ethylbenzene	0.0874	0.104	0.84
o-Xylene	0.0615	0.074	0.83
Chlorobenzene	0.0493	0.063	0.78

The ratios of the volatilization rate coefficients of each compound to that of benzene, k_v/k_v(benzene), was the same for values of k_v measured in open bioreactor air-stripping studies as reported in Table 7-2 for air-stripping studies conducted in bioreactors with air-tight lids. Table 7-6 gives a comparison of these ratios for the most volatile compounds.

TABLE 7-6

RATIOS OF VOLATILIZATION RATE COEFFICIENTS OF EACH COMPOUND TO THAT OF BENZENE

Compound	k_v/k_v(benzene) Sealed Bioreactor	k_v/k_v(benzene) Open Bioreactor
Ethylbenzene	1.16	1.14
Toluene	1.02	1.02
Benzene	1.00	1.00
o-Xylene	0.82	0.81
Chlorobenzene	0.65	0.69

The linear relationship between the first order volatilization rate coefficient, k_v, measured in the open bioreactor stripping studies and the aeration rate, Q_a, can be described by Equation 7-2. Comparisons of the results from open and sealed stripping studies, plotted as k_v versus Q_a, have been presented in Figures 7-18 to 7-22 for benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene, respectively. A summary of L, $k_{v,o}$, and the correlation coefficients from the open bioreactor volatilization studies is given in Table 7-7.

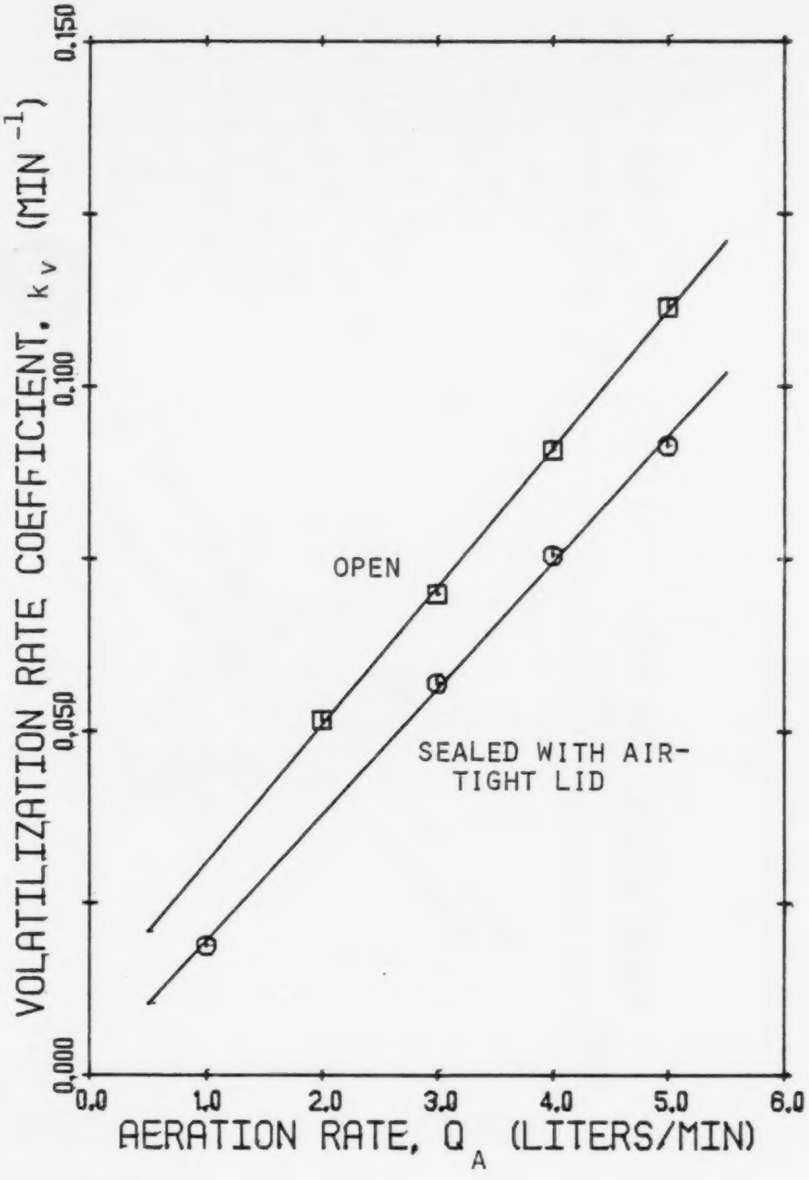


FIGURE 7-18. Data points and best-fit lines describing the relationship between the benzene volatilization rate coefficient and the aeration rate for sealed and open 10-liter bioreactors.

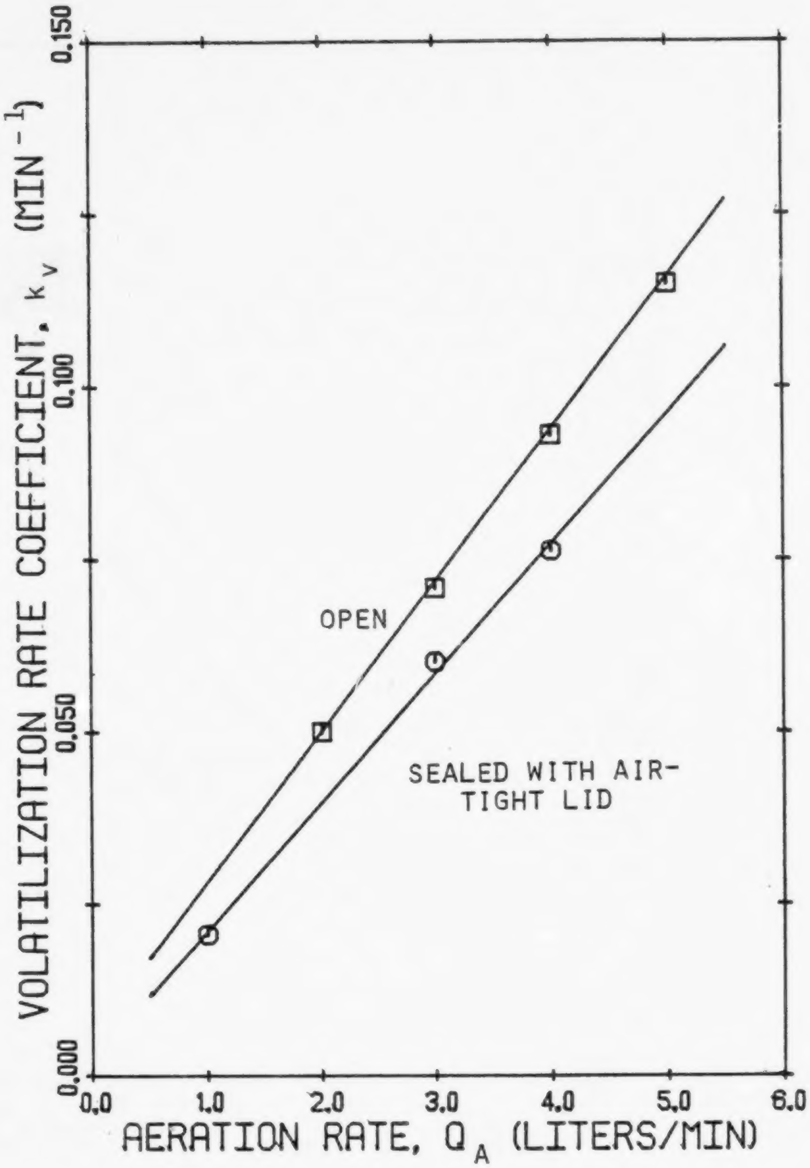


FIGURE 7-19. Data points and best-fit lines describing the relationship between the toluene volatilization rate coefficient and the aeration rate for sealed and open 10-liter bioreactors.

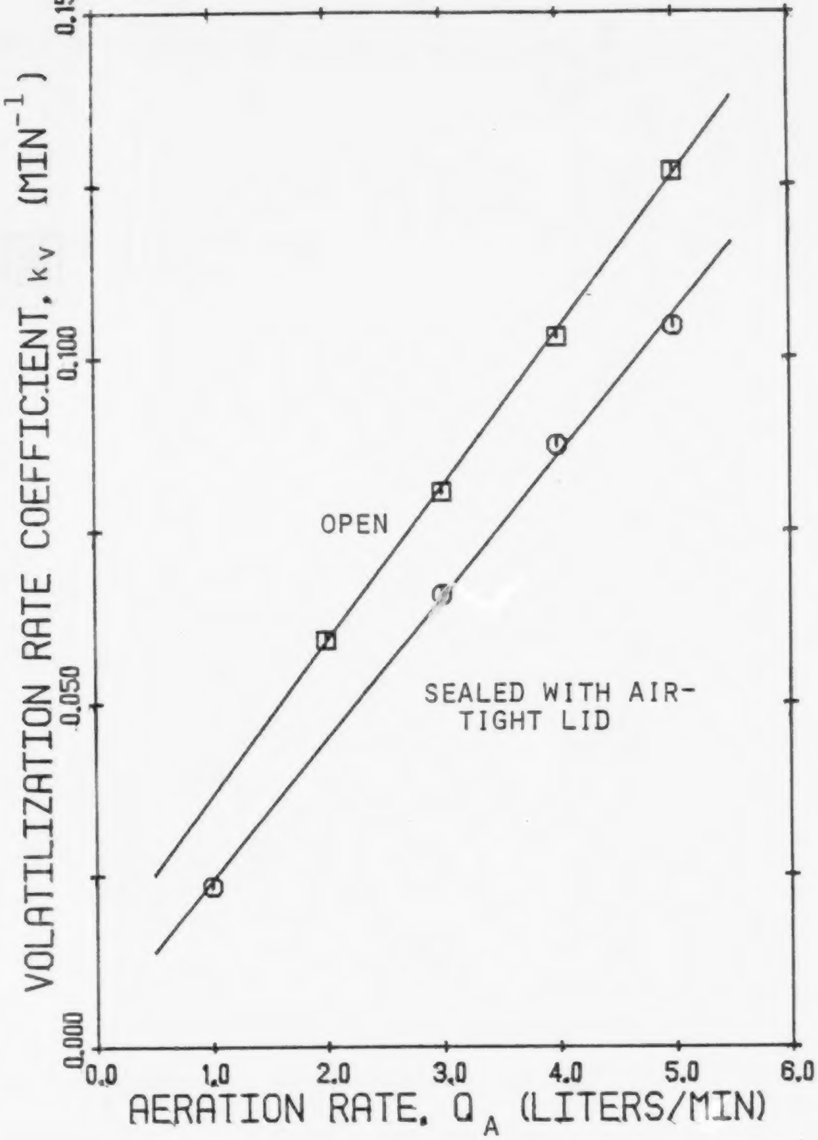


FIGURE 7-20. Data points and best-fit lines describing the relationship between the ethylbenzene volatilization rate coefficient and the aeration rate for sealed and open 10-liter bioreactors.

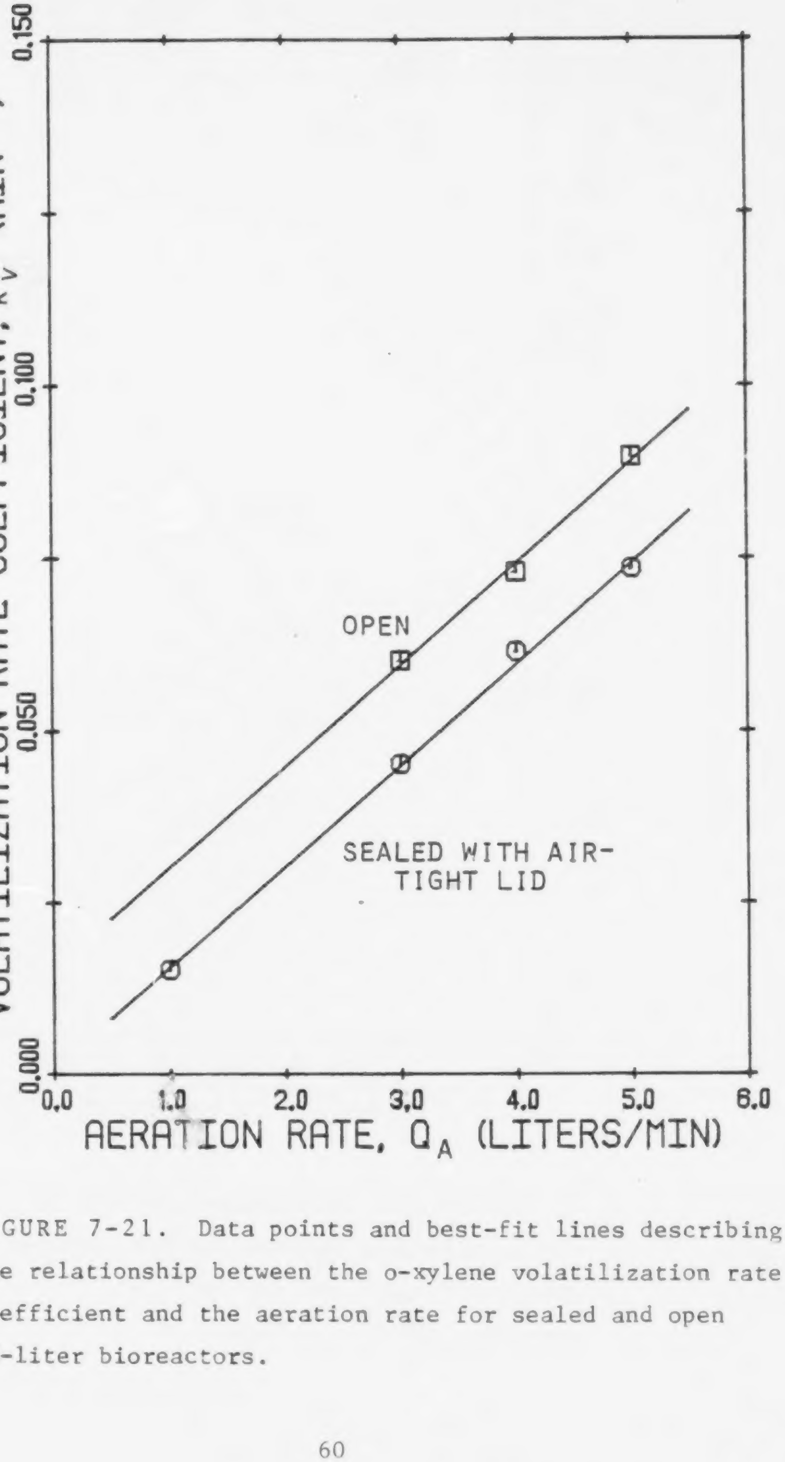


FIGURE 7-21. Data points and best-fit lines describing the relationship between the o-xylene volatilization rate coefficient and the aeration rate for sealed and open 10-liter bioreactors.

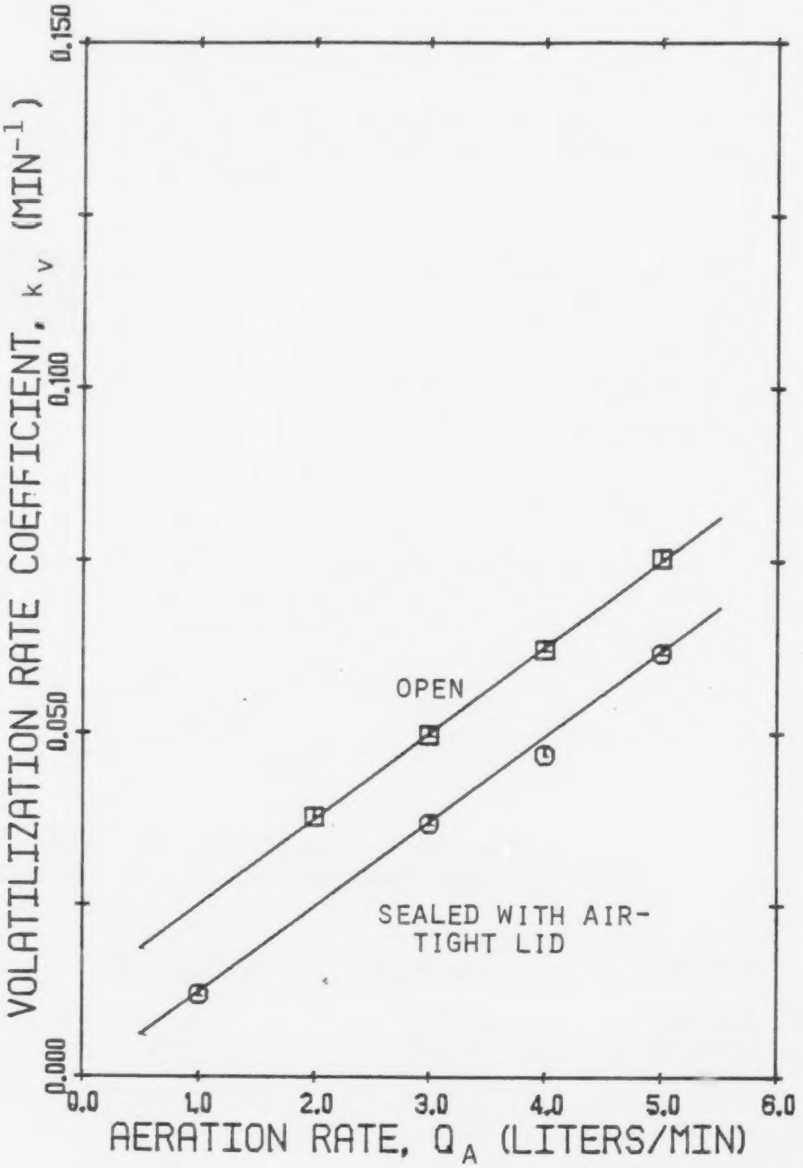


FIGURE 7-22. Data points and best-fit lines describing the relationship between the chlorobenzene volatilization rate coefficient and the aeration rate in sealed and open 10-liter bioreactors.

TABLE 7-7

VOLATILIZATION PARAMETERS RELATING k_v TO Q_a FOR AIR STRIPPING OF VOLATILE COMPOUNDS FROM 10-LITER BIOREACTORS WITHOUT AIR-TIGHT LIDS

Compound	$L(\ell^{-1})$	$k_{v,o}(\mathrm{min}^{-1})$	Corr. Coef.
Benzene	0.0200	0.0109	1.000
Toluene	0.0217	0.0063	0.999
Ethylbenzene	0.0255	0.0140	0.999
o-Xylene	0.0148	0.0153	0.999
Chlorobenzene	0.0125	0.0126	0.997

An interesting finding was that the values of L, the slope of the best-fit line through data plotted as k_v versus Q_a, was approximately the same in open and sealed bioreactor volatilization studies as shown in Table 7.8.

TABLE 7-8

COMPARISON OF L VALUES FROM SEALED AND OPEN 10-LITER BIOREACTOR VOLATILIZATION STUDIES

Compound	$L(\ell^{-1})$, Sealed	$L(\ell^{-1})$, Open	L(Sealed)/L(Open)
Benzene	0.0183	0.0200	0.92
Toluene	0.0188	0.0217	0.87
Ethylbenzene	0.0205	0.0225	0.91
O-Xylene	0.0148	0.0148	1.00
Chlorobenzene	0.0124	0.0125	0.99

7.6 OXYGEN REAERATION

The final phase of the volatilization studies was designed to evaluate the proportionality coefficients relating the rate of volatile compounds from an aqueous to gaseous phase (volatilization) to the transfer rate of oxygen from a gaseous to aqueous phase (reaeration). Various studies, including this one, have demonstrated that the volatilization rates of volatile compounds are proportional to one another (49-51). The two-film gas transfer model assumes that the rate of phase transfer of volatile compounds ($H \geq 5 \times 10^3$ atm m^3/mol) is controlled by the liquid-phase resistance. Oxygen reaeration also is controlled by the liquid-phase resistance according to this model. Therefore, oxygen can be used as a convenient reference compound to which the transfer of volatile compounds can be related. The proportionality relationship can be expressed as

$$(k_v)_i = B\ (k_L a)_{O_2} \tag{7-9}$$

where $(k_v)_i$ (min^{-1}) is the volatilization rate coefficient of an organic compound, $k_L a$ (min^{-1}) is the oxygen reaeration rate coefficient, and B is the proportionality coefficient. This principle of proportionality using oxygen as a reference compound has been demonstrated for a variety of volatile compounds over a wide range of environmental conditions (49-51). The proportionality coefficient is dependent upon the liquid phase diffusivity ratio, D_i/D_{O2}, and is relatively constant over a wide range of mixing conditions.

Oxygen reaeration rate studies were conducted in 10-liter bioreactors according to the procedure described in Section 5. Results from oxygen reaeration studies conducted at various aeration rates are presented in Figures 7-23 and 7-24. The relationship between oxygen reaeration rate coefficient, $k_L a$, and aeration rate, Q_a, shown by Figure 7-24, can be described by

$$k_L a = k_L a,_o + SQ_a \tag{7-10}$$

where $k_L a$ (min^{-1}) is the oxygen reaeration rate coefficient, $k_L a,_o$ (min^{-1}) is the calculated intercept and S (liter^{-1}) is the slope of the best-fit line relating $k_L a$ to Q_a. Values of $k_L a,_o$ and S were 0.058 min^{-1} and 0.0895 1^{-1}, respectively, and the least-squares linear regression coefficient, r^2, was 0.999.

The proportionality coefficient, B, was determined by comparing the L values for each compound to the S value for oxygen,

$$B = \frac{L}{S} \tag{7-11}$$

As seen in Table 7-9 the values of B calculated using data from sealed and open bioreactor studies do not vary significantly.

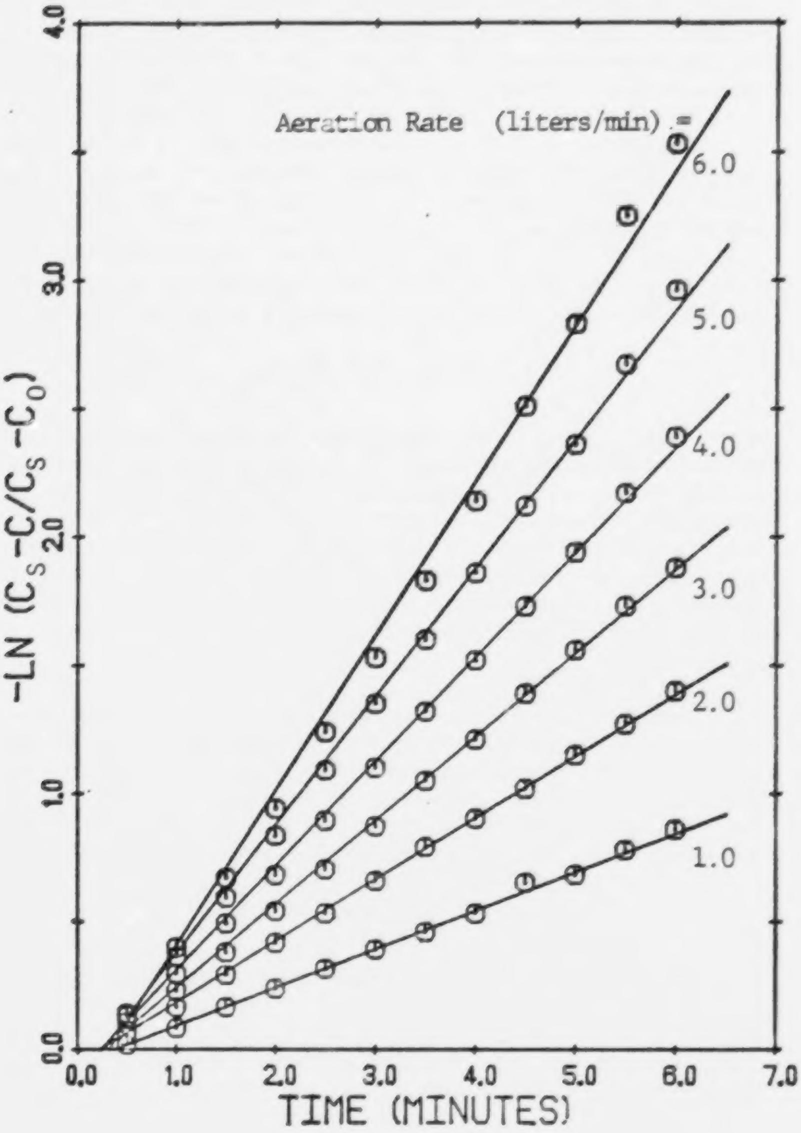


FIGURE 7-23. Experimental data and best-fit lines used to determine the oxygen reaeration rate coefficients for aeration rates from 1.0 to 6.0 liters/min in the 10-liter bioreactors without activated sludge. (20°C)

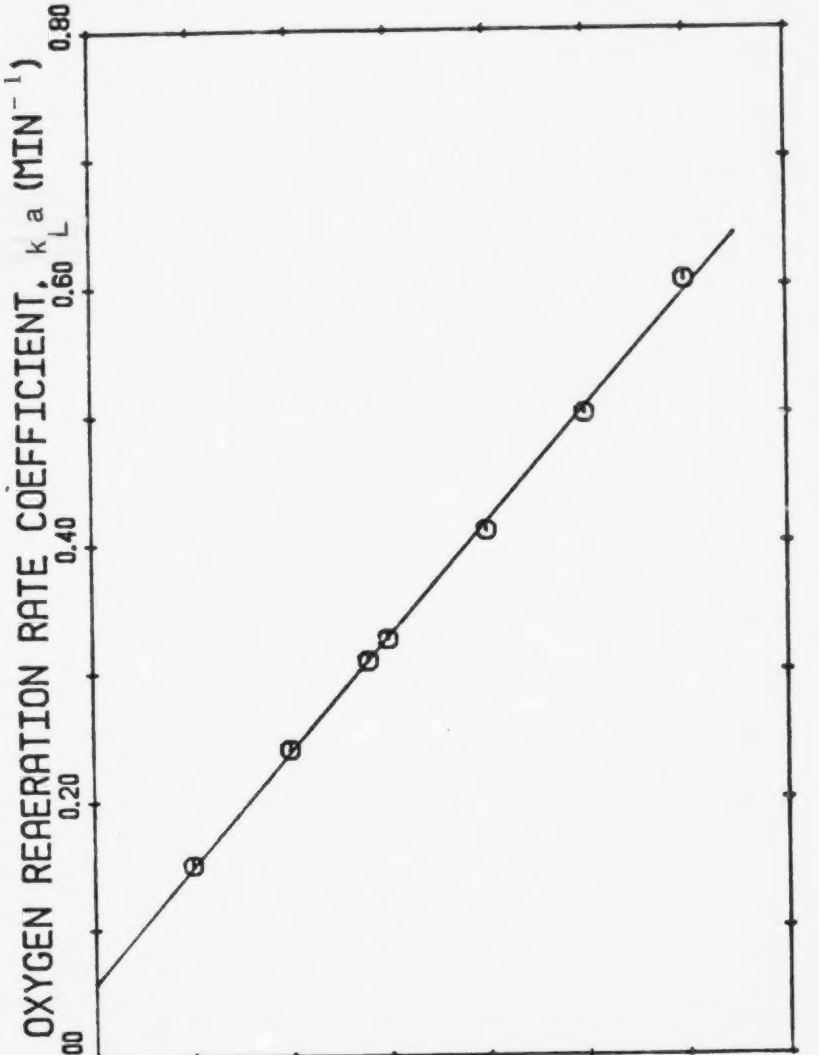


FIGURE 7-24. Experimental data and best-fit line describing the effect of aeration rate on the oxygen reaeration rate coefficient for the 10-liter bioreactors. (20°C)

TABLE 7-9

PROPORTIONALITY COEFFICIENTS RELATING VOLATILIZATION RATE COEFFICIENTS OF THE TOXIC ORGANIC COMPOUNDS TO OXYGEN REAERATION RATE COEFFICIENTS

Compound	B (Sealed Bioreactor)+	B (Open Bioreactor)++
Benzene	0.20	0.22
Toluene	0.21	0.24
Ethylbenzene	0.23	0.25
o-Xylene	0.16	0.17
Chlorobenzene	0.14	0.14
1,2-Dichlorobenzene	0.07	N.D.
1,2,4-Trichlorobenzene	0.07	N.D.

N.D. = Not Determined

+ Bioreactors with air-tight lids

++ Bioreactors without lids

SECTION 8

RESULTS: BIOSORPTION STUDIES

Rate and equilibrium studies were conducted to evaluate the importance of biosorption as a removal mechanism during activated sludge treatment. The three compounds used in the biosorption experiments, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane were selected because they have the largest octanol/water partition coefficients, K_{ow}. Various studies have shown that the degree of bioaccumulation of hydrophobic organics by fish and other aquatic organisms increases with increasing values of K_{ow}(52,53).

8.1 RATE STUDIES

Sorption rate studies were conducted with lindane to evaluate the time required to reach equilibrium conditions. The studies were performed in 2.6-liter glass completely-mixed batch reactors stirred with a teflon paddle attached to a glass stirring rod. The sorbent used was mixed liquor suspended solids from a bioreactor not receiving toxic organics in the influent. After transferring 2.6 liters of mixed liquor to the CMB reactor, the contents of the CMB reactor were spiked with 10 μℓ of methanol containing lindane. Samples were taken with a 10-mℓ syringe, filtered through 25 mm glass fiber filters, and extracted with hexane.

Results from a sorption rate study presented in Figure 8-1 show a rapid uptake of lindane by the bacteria. Equilibrium conditions were achieved within 15 to 20 minutes. At the end of 130 minutes mixed liquor samples containing both the solid and aqueous phases were extracted for lindane. The result yielded a complete recovery of lindane indicating that sorption was a reversible process and that removal was not attributable to biodegradation.

8.2. EQUILIBRIUM RESULTS

The sorption equilibrium experiments were performed with settled activated sludge with a known suspended solids concentration from an activated sludge bioreactor not receiving toxic organic compounds in the influent. Various volumes of the settled sludge were added to 150 mℓ hypo-vials® and diluted to 150 mℓs to eliminate headspace and minimize volatilization. Each vial was spiked with a toxic organic compound in a

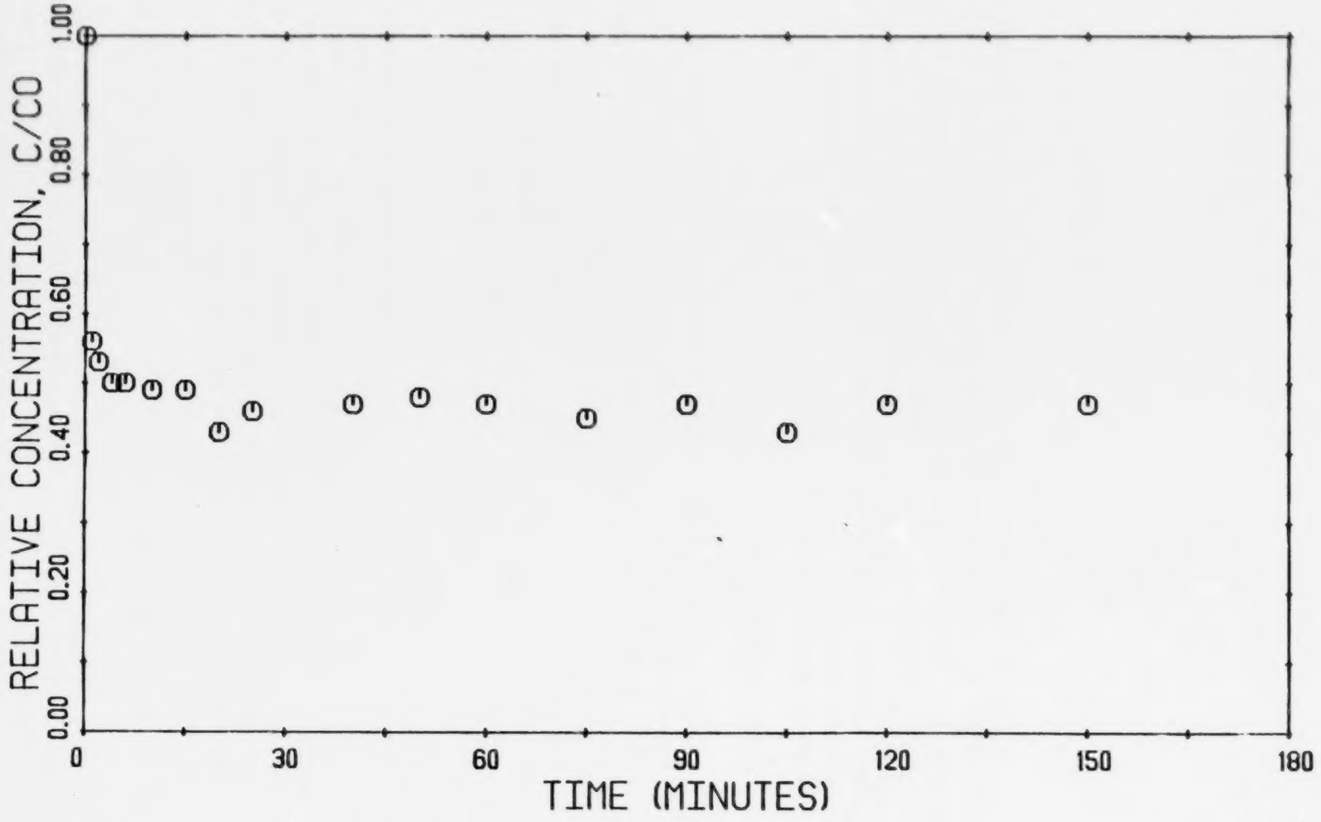


FIGURE 8-1. Sorption of lindane by activated sludge mixed liquor suspended solids in a completely mixed batch (CMB) reactor. (C_o = 84 ug/l and MLSS = 3800 mg/l)

methanol carrier, sealed, and mixed with a magnetic stirrer for 3 hours. Samples from each vial were centrifuged, and the supernatant was extracted with hexane.

Freundlich and Linear Phase Partitioning isotherm models were used to evaluate the data from the biosorption experiments. The Freundlich model has the form

$$q_e = K_f C_e^{1/n} \qquad (8\text{-}1)$$

where q_e (μg sorbed/mg MLSS) is the amount of solute removed per unit weigh of sorbent, C_e (μg/ℓ) is the equilibrium solution concentration, and K_f and $1/n$ are characteristic constants. The Freundlich model linearizes in logarithmic form:

$$\log q_e = \log K_f + 1/n \log C_e \qquad (8\text{-}2)$$

Figure 8-2 shows the sorption data and best-fit lines for the Freundlich model. As expected, 1,2,4-trichlorobenzene showed a greater degree of sorption than lindane due to the higher octanol/water partition coefficient. Values of K_f and $1/n$ are given in Table 8-1.

The Linear Phase Partitioning model for biosorption has the form:

$$q_e = K_p C_e \qquad (8\text{-}3)$$

where K_p, the partition coefficient, is the ratio of the amount sorbed to the equilibrium solution concentration. A similar model, in which K_p is replaced by $K_B/10^6$, has been used for describing the bioconcentration of hydrophobic compounds by aquatic organisms (52,53). K_B is the bioconcentration factor. Plots of the amount sorbed versus the equilibrium solution concentration in Figure 8-3 revealed a reasonably linear phase partitioning. The characteristic constants and the correlation coefficients for the Linear Partitioning model are given in Table 8-1. Results from the biosorption equilibrium studies showed that the bioconconcentration factor, K_B, for 1,2,4-trichlorobenzene was greater than that for lindane.

8.3. CORRELATION OF K_B WITH K_{ow}

Various studies have attempted to correlate bioconcentration with other physical parameters. Work by Neely (54), Veith (52), and Mackay (53) have shown that bioconcentration of hydrophobic organic compounds

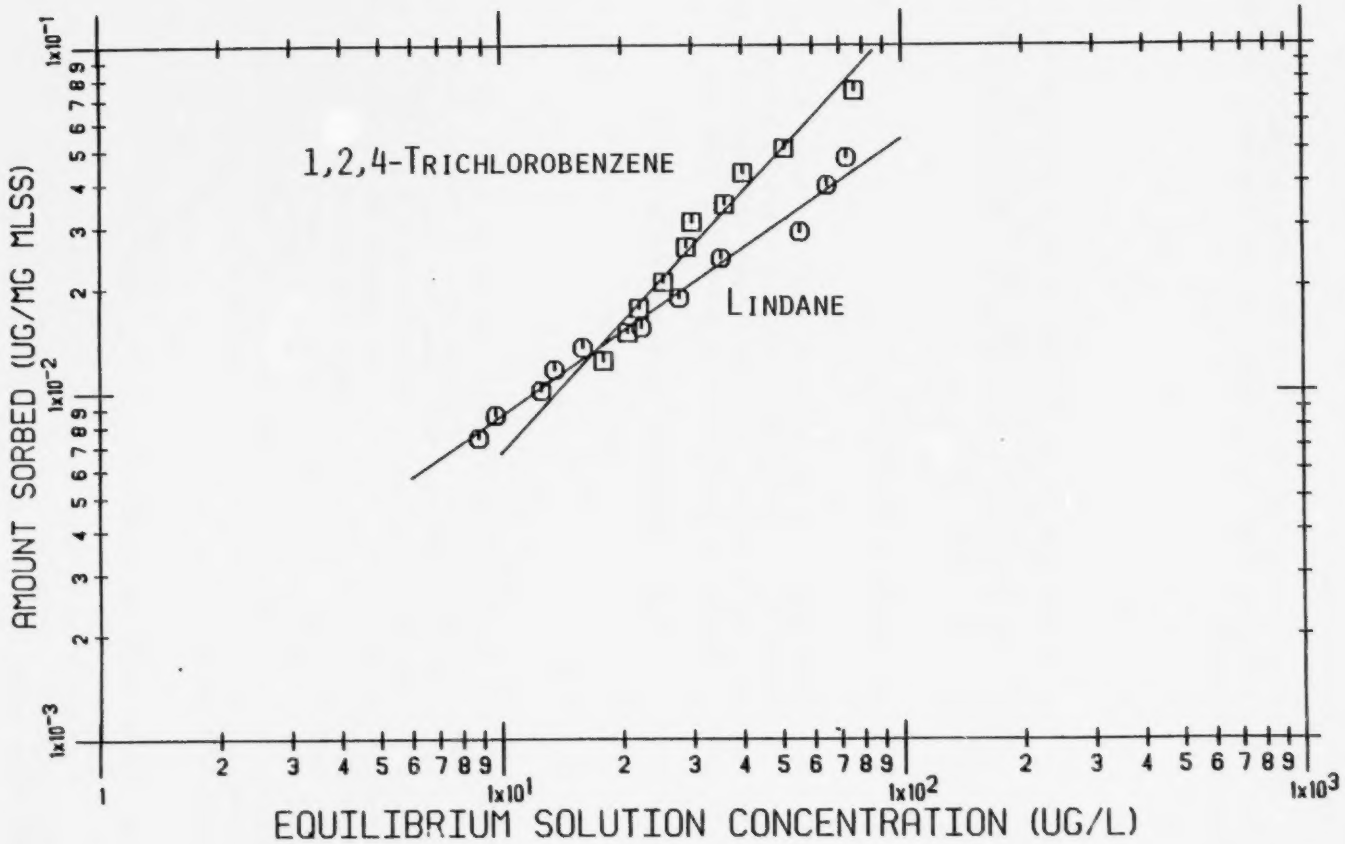


FIGURE 8-2. Freundlich isotherms for the sorption of lindane and 1,2,4-trichlorobenzene by activated sludge mixed liquor suspended solids.

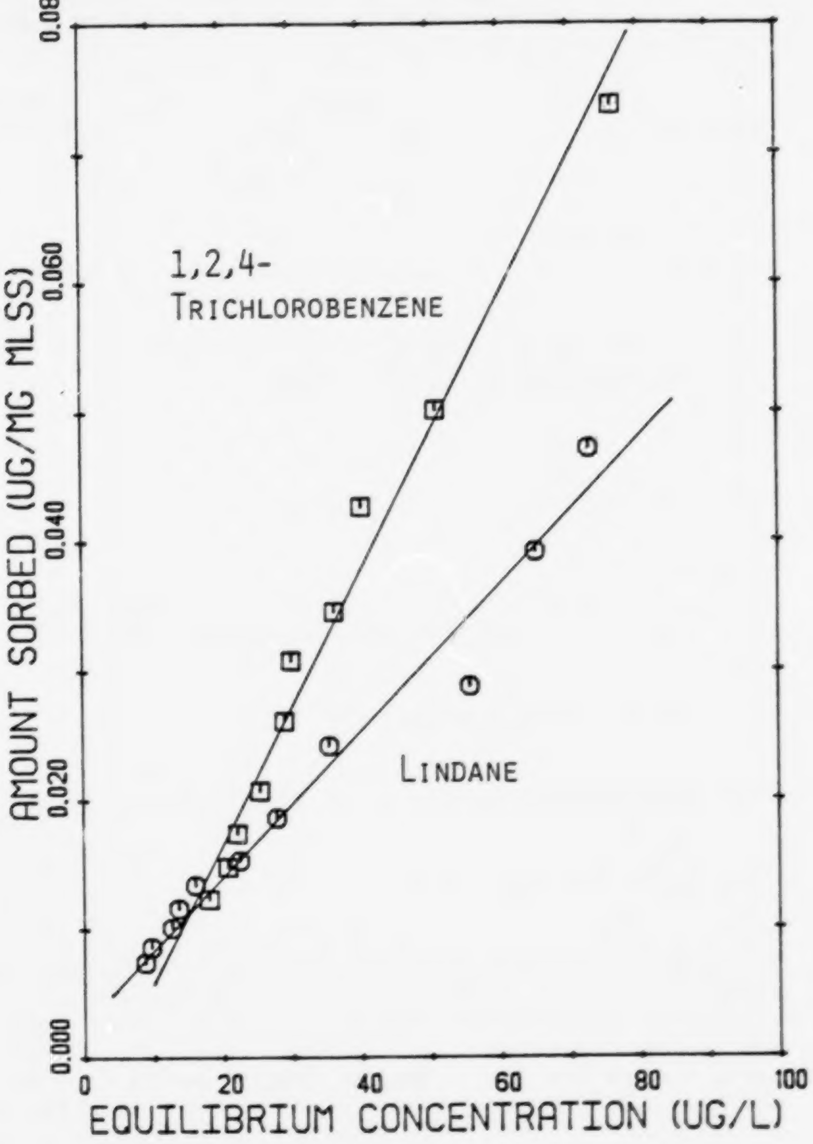


FIGURE 8-3. Linear partioning isotherms for the sorption of lindane and 1,2,4-trichlorobenzene by activated sludge mixed liquor suspended solids.

TABLE 8-1

ISOTHERM MODEL PARAMETERS FOR SORPTION OF TOXIC ORGANIC COMPOUNDS BY ACTIVATED SLUDGE

	Linear		Freundlich$^+$		
Compound	K_B	Corr.	K_f^{++}	1/n	Corr.
Lindane	568	0.987	0.0014	0.789	0.992
1,2,4-Trichlorobenzene	1030	0.991	0.00039	1.24	0.987

+ Evaluated using C_e in µg/ℓ and q_e in µg/mg MLSS

++ Intercept at C_e = 1.0 µg/ℓ

can be correlated to the octanol/water partition coefficient. Veith (52) found the following equation described this relationship

$$\log K_B = 0.85 \log K_{ow} - 0.70 \quad (8\text{-}4)$$

while Mackay (53) suggested a one parameter correlation

$$\log K_B = \log K_{ow} - 1.32 \quad (8\text{-}5)$$

The lines described by equations 8-4 and 8-5 were plotted in Figure 8-4 along with results from this study and data reported by Mackay (53) and Veith (52) for representative toxic, organic compounds. Data given by Mackay (53) and Veith (52) came from various bioconcentration studies using fish as the test organisms, while results from this study were obtained with activated sludge mixed liquor biological suspended solids as the test organisms. The results from this study agreed quite well with results from other bioconcentration studies. As shown by the comparison in Table 8-2, lindane and 1,2,4-trichlorobenzene bioconcentration factors were approximately the same in this study as were reported by Veith (52). Such correlations are useful for

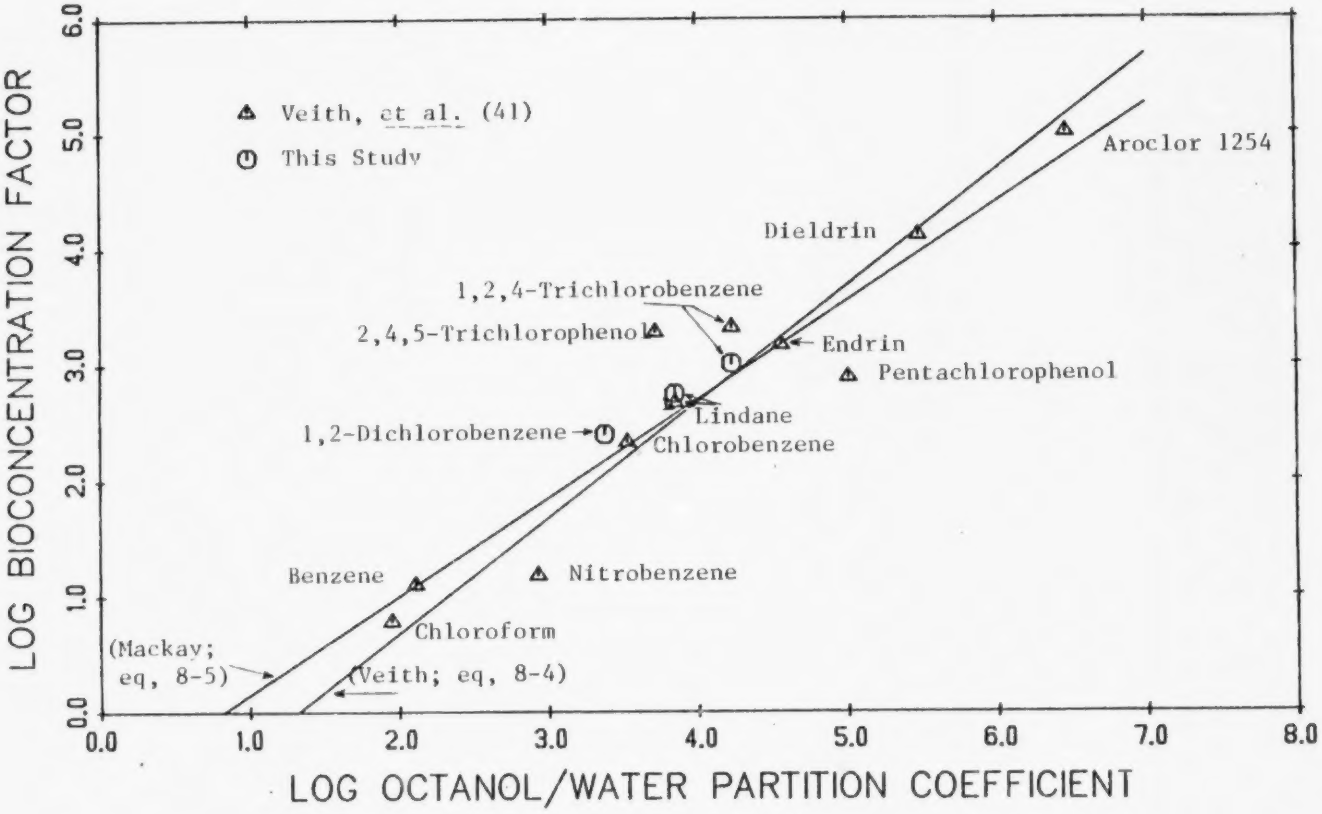


FIGURE 8-4. Correlation between the bioconcentration factor and octanol/water partition coefficient for selected hydrophobic organic compounds.

estimating the degree to which specific compounds are likely to be removed by biosorption during activated sludge treatment since octanol/water partition coefficients are available for many environmentally important organic compounds. Assuming equilibrium conditions exist between the sorbed and aqueous concentrations, as the results shown in Figure 8-1 suggest, the amount of a compound sorbed by the activated sludge biomass can be quantified for any set of operating conditions encountered in activated sludge processes.

TABLE 8-2

COMPARISON OF K_B VALUES FROM THIS STUDY TO THOSE REPORTED BY VEITH, *ET AL.* (52)

Compound	Log K_{ow}	Log K_B This Study	Log K_B Veith et al. (41)
Lindane	3.85	2.75	2.67
1,2,4-Trichlorobenzene	4.23	3.01	3.32

SECTION 9

DEVELOPMENT OF TRACE ORGANICS REMOVAL MODEL FOR ACTIVATED SLUDGE

9.1. Introduction

Current models for the removal of soluble organics during wastewater treatment typically originate from the traditional substrate mass balance equation which has the form

$$V\left(\frac{dC}{dt}\right) = Q_i C_i - Q_e C_e + V\left(\frac{dC}{dt}\right)_B \qquad (9\text{-}1)$$

Change of mass in reactor	=	mass entering reactor in influent	-	mass leaving reactor in effluent	+	change of mass due to biodegradation

Such a mass balance does not include removal mechanisms of air-stripping and biosorption, and therefore cannot accurately predict the fate of a wide variety of toxic organic compounds. A more complete substrate mass balance which includes the three dominant trace organic removal mechanisms of volatilization, biodegradation and biosorption has the form

$$V\left(\frac{dC}{dt}\right) = Q_i C_i - Q_e C_e + V\left(\frac{dC}{dt}\right)_V + V\left(\frac{dC}{dt}\right)_S + V\left(\frac{dC}{dt}\right)_B \qquad (9\text{-}2)$$

Change of mass in reactor	=	mass entering reactor in influent	-	mass leaving reactor in effluent	+	change of mass due to air stripping	+	change of mass due to biosorption	+	change of mass due to biodegradation

This equation when applied to steady-state operating conditions becomes the Steady-State Trace Organics Removal Model (STORM) for activated sludge. The following sections present development of the model for various classifications of toxic organic compounds based upon their physical and biochemical properties.

9.2. GENERAL STORM DEVELOPMENT

9.2.1. Air Stripping

The air-stripping of a volatile trace organic can be conveniently represented by the first-order removal expression

$$\left(\frac{dC}{dt}\right)_v = -k_v C \qquad (9\text{-}3)$$

as was detailed in Section 7.

9.2.2. Biosorption

Results presented in Section 8 suggest that biosorption is controlled by equilibrium rather than mass transfer rate considerations. The biosorption term can be based upon an assumption that equilibrium exists between the solution and sorbed phase concentrations of a toxic organic. That equilibrium condition can be represented as

$$q_e = K_p C_e \qquad (9\text{-}4)$$

The term in the CMF reactor mass balance equation representing the mass removed by biosorption can be written as $q_e M_s Q_s$, where q_e(μg/mg) is sorbed concentration of a toxic organic, M_s(mg/ℓ) is the mixed liquor suspended solids concentration and Q_s(ℓ/min) is the sludge waste removal rate.

9.2.3.. Biodegradation

The biodegradation of a trace organic compound can be represented as a pseudo first order removal expression represented as

$$\left(\frac{dC}{dt}\right)_B = -k_b C \qquad (9\text{-}5)$$

where $k_b(\text{min}^{-1})$ is the pseudo first order biodegradation rate coefficient.

Substituting for each of the removal terms in equation (9-2) yields

$$V\left(\frac{dC}{dt}\right) = Q_iC_i - Q_eC_e - Vk_vC - Vk_bC - q_eM_sQ_s \qquad (9\text{-}6)$$

which can be simplified under conditions of steady-state to

$$Q_iC_i = Q_eC_e + Vk_vC_e + Vk_bC_e + q_eM_sQ_s \qquad (9\text{-}7)$$

This model can be used to predict the fate of toxic organic compounds during activated sludge treatment if basic information about the individual removal mechanisms is known.

9.3. APPLICATION OF STORM TO NON-BIODEGRADABLE COMPOUNDS

The removal of non-biodegradable compounds can occur as a result of volatilization and biosorption as indicated by equation 9-8.

$$Q_iC_i = Q_eC_e + Vk_vC_e + q_eM_sQ_s \qquad (9\text{-}8)$$

Depending upon the physical properties of a compound one or the other removal mechanisms may dominate. Non-biodegradable compounds with large values of Henry's constant and small biosorption coefficients will likely be removed by air-stripping while compounds with small Henry's constants and large biosorption coefficients will be sorbed by the biomass. Compounds in an intermediate range may be subject to removal by a combination of the two mechanisms. Consideration will be given to volatilization as the dominant removal mechanism, then biosorption as the dominant mechanism, and finally a combination of the two.

9.3.1. Volatilization

The mass balance equation for conditions of steady-state that represent the air-stripping of a volatile, non-biodegradable and non-biosorbable compound is:

$$Q_iC_i = Q_eC_e + Vk_vC_e \qquad (9\text{-}9)$$

where Q_iC_i is the influent mass flux, N_o, Q_eC_e is the effluent mass flux, N_e, and Vk_vC_e is the off-gas mass flux, N_g. In the context of this work the amounts of a compound stripped to the atmosphere were not regarded as ultimately removed, but rather redistributed. The off-gas mass flux can also be written as the product of the concentration of a compound in the off-gas, C_g, and the off-gas flow rate, Q_g:

$$N_g = Vk_vC_e = C_gQ_g \tag{9-10}$$

The effluent and off-gas concentrations of volatile non-biodegradable poorly sorbed compounds can be predicted by the following equations developed in Section 7:

$$Ce = \frac{C_i}{1+k_v\bar{t}} \tag{9-11}$$

$$C_g = \frac{VC_ek_v}{Q_g} \tag{9-12}$$

The ratio of effluent to influent concentrations, C_e/C_i, has been plotted as a function of k_v in Figure 9-1 for a 5.5 hour hydraulic retention time, $\bar{t}$. The circles represent values of k_v calculated for the volatile compounds by Equation 7-2 for an aeration rate of 4.0 ℓ/min. A 90% reduction in the aqueous concentration occurs for compounds with values of k_v greater than 0.025 min^{-1}. As shown in Figure 9-1, over 90% of the influent mass flux will leave the bioreactors in the off-gas for non-biodegradable compounds with volatilization rate coefficients greater than 0.025 min^{-1}. Both 1,2-dichlorobenzene and 1,2,4-trichlorobenzene have volatilization coefficients of about 0.025 min^{-1} at an aeration rate of 4.0 ℓ/min. Approximately one third of the organic priority pollutants can be considered to have relative volatilities equal to or greater than 1,2,4-trichlorobenzene.

The sensitivity of air-stripping removal to the hydraulic retention time, $\bar{t}$, has been shown by Figure 9-2 to be small. A decrease in the hydraulic retention time by nearly 50% to 3.0 hours still results in at least an 85% reduction in the aqueous concentration for compounds with relative volatilities greater than or equal to 1,2-dichlorobenzene.

9.3.2. Biosorption

A steady-state mass balance equation for non-biodegradable, non-volatile compounds that are removed by biosorption has the form

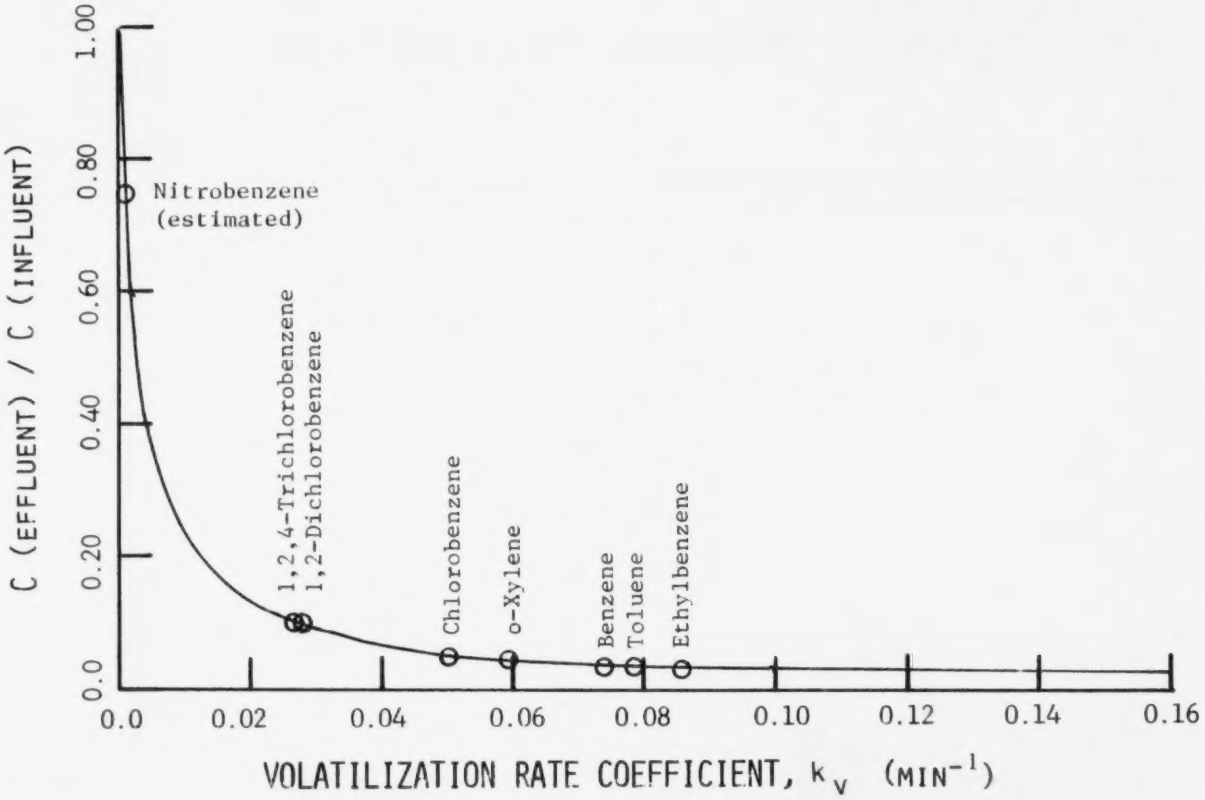


FIGURE 9-1. Relationship between the volatilization rate coefficient and the reduction in aqueous concentration of volatile compounds in 10-liter bioreactors with air-tight lids.

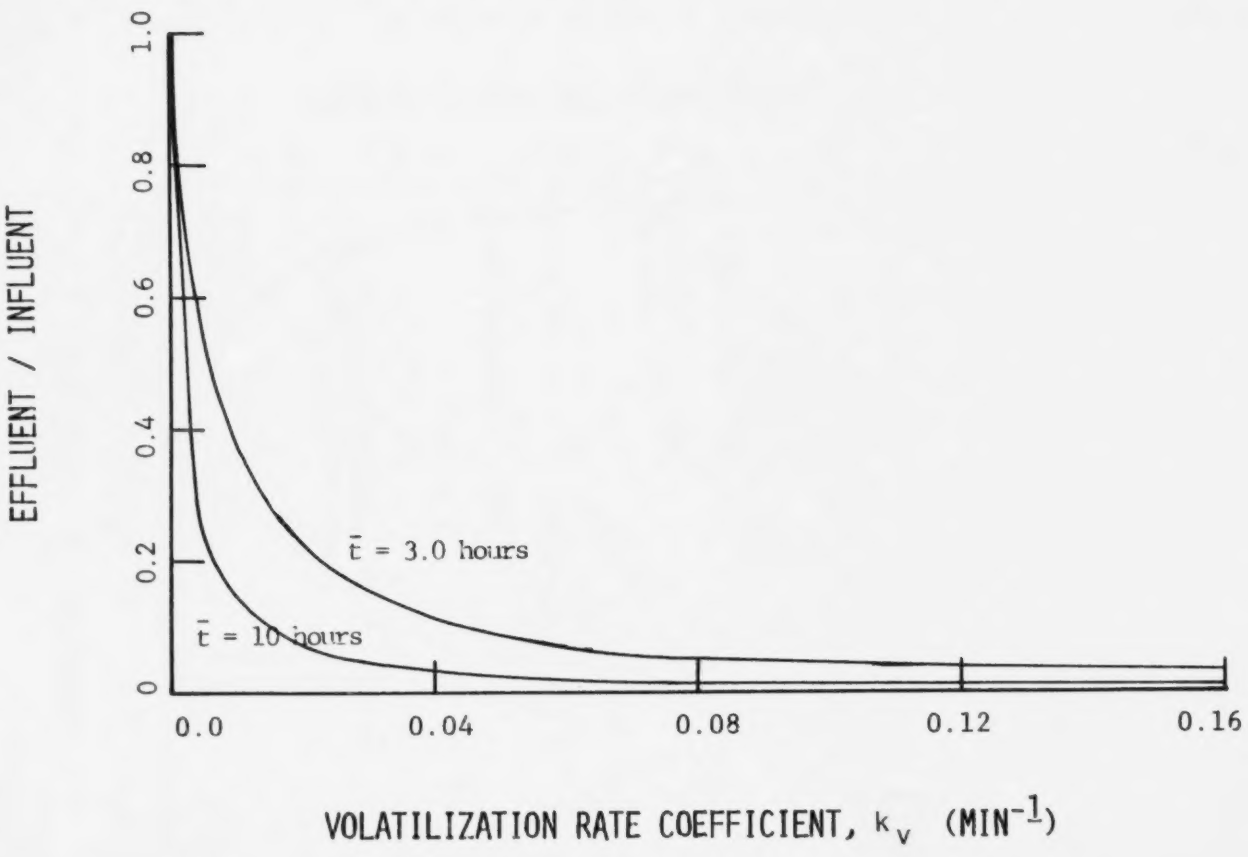


FIGURE 9-2. Sensitivity of the air-stripping model to changes in the hydraulic retention time in 10-liter bioreactors.

$$Q_iC_i = Q_eC_e + q_eM_sQ_s \tag{9-13}$$

Substituting for q_e in Equation 9-13 gives

$$Q_iC_i = Q_eC_e + K_pC_eM_sQ_s \tag{9-14}$$

The sludge waste flow from the experimental bioreactors was small and the effluent flow was approximately equal to the influent flow. In addition, sludge was wasted directly from the aeration basin section of the bioreactors. Therefore Equation 9-14 can be rearranged and written as

$$\frac{C_e}{C_i} = \left[1+\frac{\bar{t}K_pM_s}{(24)SRT}\right]^{-1} \tag{9-15}$$

where SRT (days) is the mean solids retention time.

Results presented in Section 8 showed that the bioconcentration factor K_B for the compounds used in this project were similar to those obtained for other test organisms. The value of K_p must be multiplied by 10^6 to convert the units (μg/mg)/(μg/ℓ) to a dimensionless form. Substituting the bioconcentration factor, K_B, for K_p in Equation 9-15 gives

$$\frac{C_e}{C_i} = \left[1 + \frac{\bar{t}M_sK_B10^{-6}}{(24)SRT}\right]^{-1} \tag{9-16}$$

Various studies have shown that a reasonably good correlation exists between the bioconcentration factor and the octanol/water partition coefficient, K_{ow}, which is generally more available than values of K_B. While numerous correlations have been suggested, the single constant correlation given by Mackay (53) of

$$K_B = 0.048K_{ow} \tag{9-17}$$

is the simplest. After substituting K_{ow} for K_B, Equation 9-16 can be written

$$\frac{C_e}{C_i} = \left[1 + \frac{\bar{t} M_s K_{ow} 2 \times 10^{-9}}{SRT} \right]^{-1} \qquad (9\text{-}18)$$

The removal of a hydrophobic, non-volatile, non-biodegradable compound by biosorption can be predicted by Equation 9-18 for any set of activated sludge operating conditions.

Equation 9-18 was solved as a function of K_{ow} and the results in Figure 9-3 are given as C_e/C_i versus Log K_{ow} for operating conditions of M_s = 3500 mg MLSS/ℓ, SRT = 6 days and $\bar{t}$ = 5.5 hours. The results indicate that biosorption will not significantly affect the aqueous concentration of compounds with Log K_{ow} values less than 4.0. Predicted removals are given for specific non-volatile compounds assuming biodegradation does not occur. Equation 9-18 predicts a 45% removal for compounds with Log K_{ow} values of 5.0 and 90% removals for compounds with Log K_{ow} values greater than 6.0.

Results presented in Figure 9-4 show how the concentration of MLSS affects the removal of trace organics by sorption for an activated sludge operated at hydraulic and solids residence times of 5.5 hours and 6 days, respectively. The lines represent predicted removals for constant values of K_{ow}. For a compound with a Log K_{ow} value of 5.0 removals at steady-state MLSS concentrations of 3000 and 4000 mg/ℓ are predicted to be approximately 35 and 45%, respectively.

9.3.3. Volatilization and Biosorption

The steady-state equation for non-biodegradable compounds that are removed by volatilization and biosorption has the form

$$Q_i C_i = Q_e C_e + V k_v C_e + q_e M_s Q_s \qquad (9\text{-}19)$$

Using the same substitutions as previously described for the individual removal mechanisms, Equation 9-19 can be written as

$$\frac{C_e}{C_i} = \left[1 + \bar{t} k_v + \frac{\bar{t} M_s K_B \times 10^{-6}}{(24) SRT} \right]^{-1} \qquad (9\text{-}20)$$

The bioconcentration factor, K_B, can be replaced by the octanol/water partition coefficient, K_{ow}, using the relationship suggested by Mackay (53), and Equation 9-20 can be rewritten as

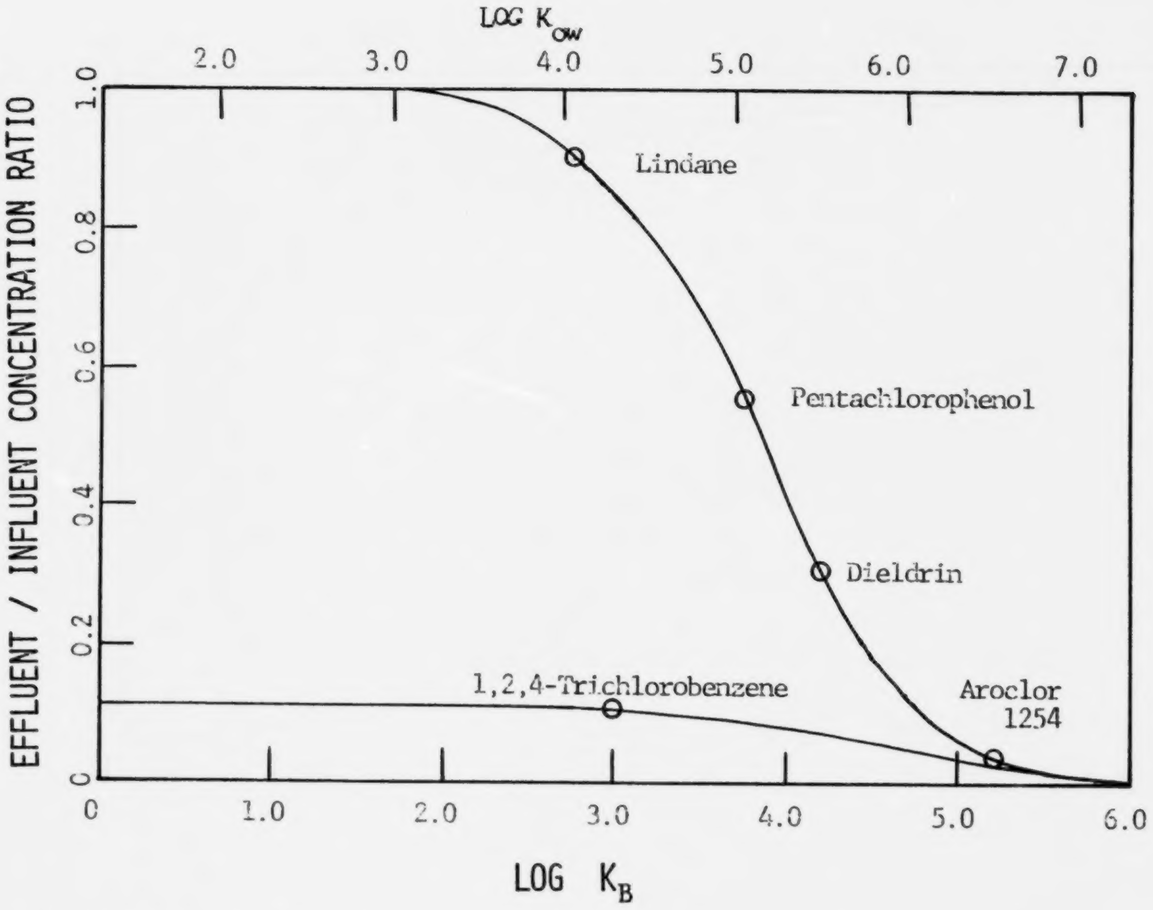


FIGURE 9-3. Relationship between the biosorption coefficient and the reduction in aqueous concentration of hydrophobic organic compounds due to sorption by activated sludge.

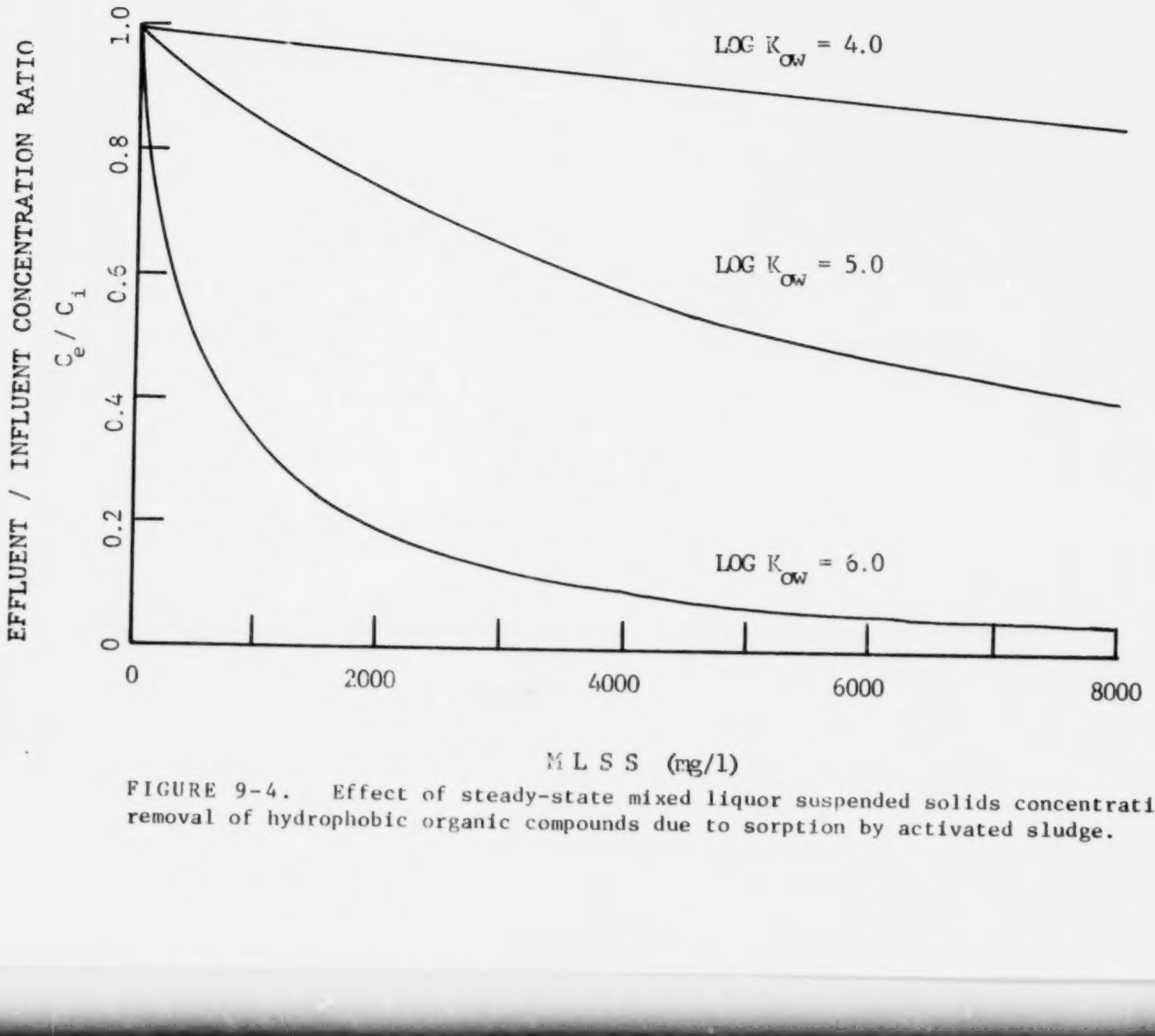


FIGURE 9-4. Effect of steady-state mixed liquor suspended solids concentration on removal of hydrophobic organic compounds due to sorption by activated sludge.

$$\frac{C_e}{C_i} = \left[1 + \bar{t}\, k_v + \frac{\bar{t} M_s K_{ow} 2\text{x}10^{-9}}{SRT} \right]^{-1} \qquad (9\text{-}21)$$

The effluent to influent concentration ratio C_e/C_i, in Equation 9-21 was solved as a function of log K_{ow} for various values of k_v, and the results have been plotted in Figure 9-5. As volatility increases, the effect of biosorption on the overall reduction in the aqueous concentration is significantly reduced. The predicted reduction in the aqueous concentration of 1,2,4-trichlorobenzene shown in Figure 9-5 indicates that removal due to biosorption will be insignificant compared with volatilization.

9.4 APPLICATION OF STORM TO BIODEGRADABLE COMPOUNDS

A variety of the organic priority pollutants have been reported to be potentially biodegradable in controlled laboratory studies by microorganisms typically found in activated sludge. Many of these compounds are characterized by Henry's constants that indicate high volatility in activated sludge systems and/or octanol/water partition coefficients that suggest the potential for biosorption. Therefore, the removal of biodegradable compounds from a CMF activated sludge system, operated under conditions of steady-state can be expressed as

$$Q_i C_i = Q_e C_e + V k_b C_e + V k_v C_e + q_e M_s Q_s \qquad (9\text{-}22)$$

Depending on the relative magnitude of the various removal terms one of the removal mechanisms may dominate and control the fate of a trace toxic organic compound during activated sludge treatment. Consideration will be given to removal mechanisms of biodegradation and volatilization.

9.4.1. Biodegradation

The steady-state equation for the removal of non-volatile, nonbiosorbable trace organics by biodegradation can be written

$$Q_i C_i = Q_e C_e + V k_b C_e \qquad (9\text{-}23)$$

Solving equation 9-23 for the effluent concentration, C_e, gives

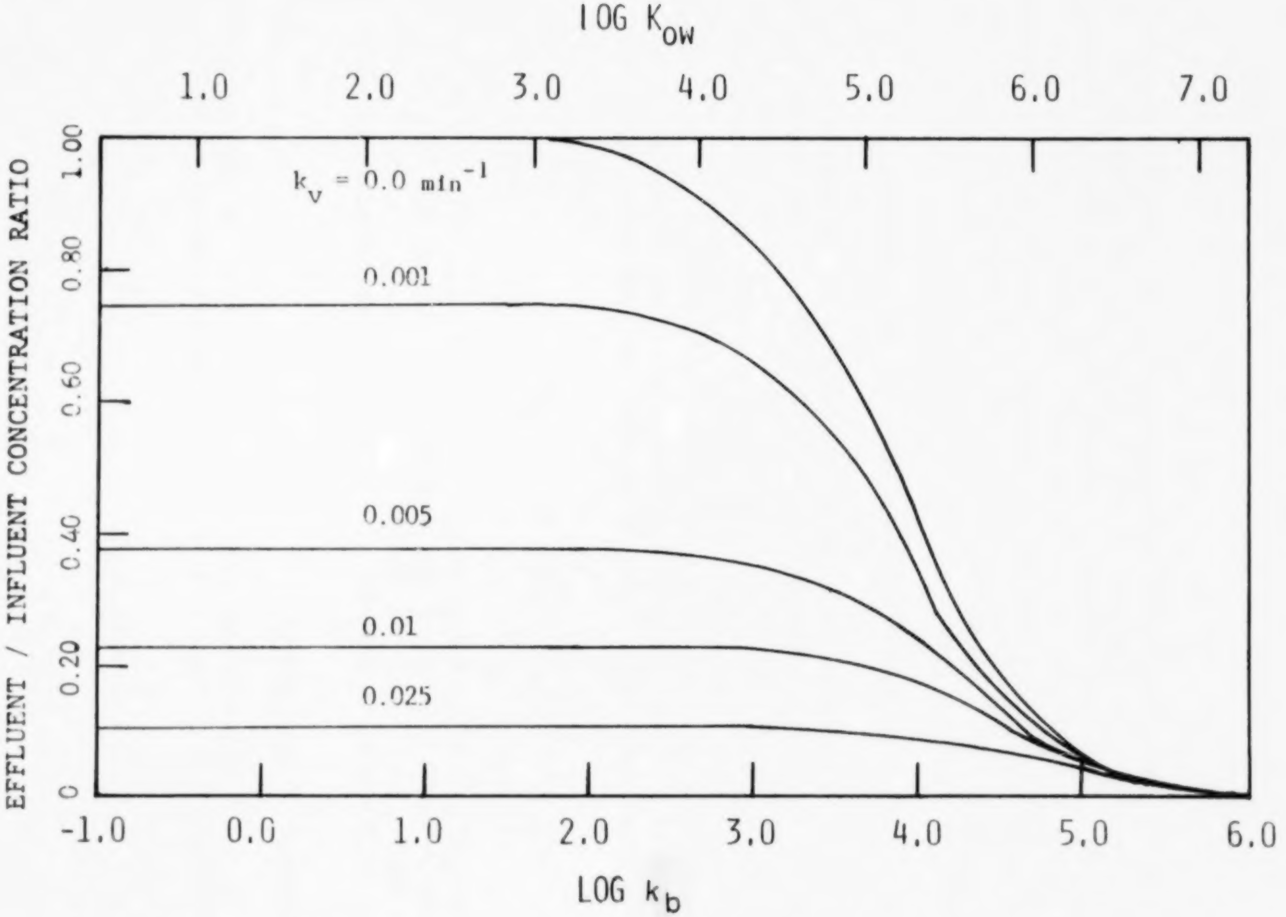


FIGURE 9-5. Effect of increasing volatilization rate coefficients on the removal of hydrophobic compounds due to sorption by activated sludge.

$$C_e = \frac{C_i}{1+k_b\bar{t}} \qquad (9\text{-}24)$$

The effluent/influent concentration ratio C_e/C_i, has been solved for a hydraulic retention time of 5.5 hours and the results plotted in Figure 9-6. The resulting curve has the same shape as the one representing removal due to air-stripping in Figure 9-1. An 80% reduction in the aqueous concentration is predicted for compounds with biodegradation rate coefficients, k_b, of approximately 0.1 min^{-1}.

9.4.2. Biodegradation and Volatilization

This situation represents one of the most interesting combinations of removal mechanisms, and the mass balance equation for conditions of steady-state which incorporates removal mechanisms of biodegradation and volatilization can be written as

$$Q_iC_i = Q_eC_e + Vk_vC_e + Vk_bC_e \qquad (9\text{-}25)$$

While many organic priority pollutants classified as purgeable have been shown to be biodegradable, removal of trace concentrations (microgram-per-liter) of these compounds has been attributed primarily to air-stripping.

With the appropriate substitutions, Equation 9-25 can be rearranged and written as

$$\frac{C_e}{C_i} = \left[1+\bar{t}(k_v+k_b)\right]^{-1} \qquad (9\text{-}26)$$

A more complete method of predicting the fate of volatile, biodegradable compounds which incorporates off-gas mass fluxes into the mass balance expression can be written as

$$Q_iC_i = Q_eC_e + Q_gC_g + Vk_bC_e \qquad (9\text{-}27)$$

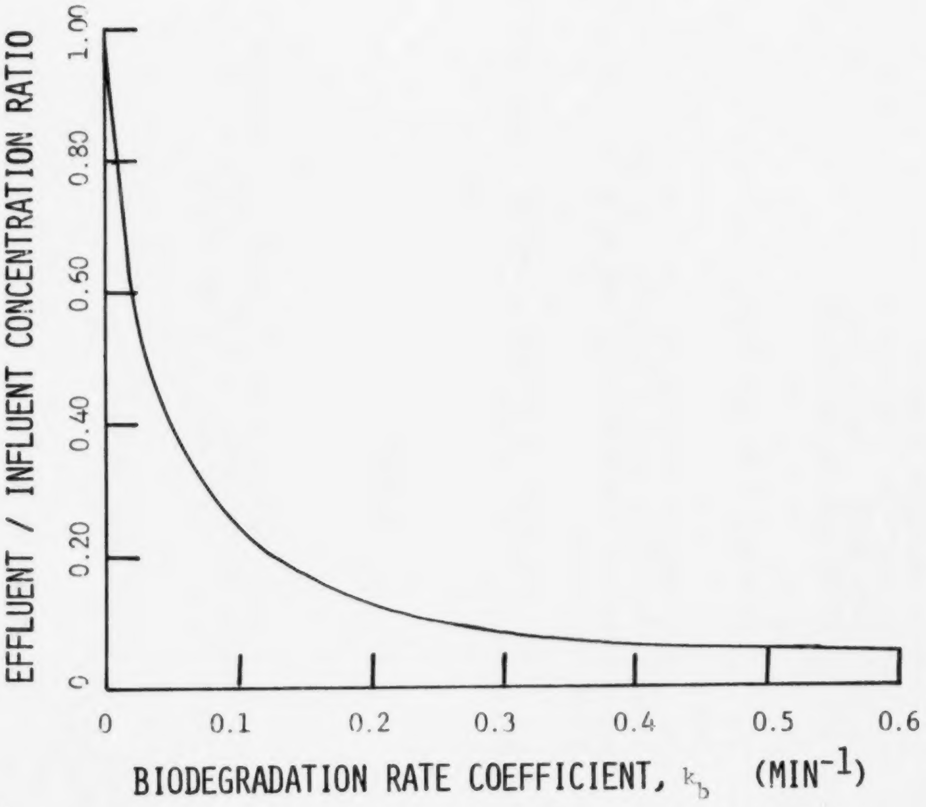


FIGURE 9-6. Relationship between the biodegradation rate coefficient and the reduction in aqueous concentration of a non-volatile compound.

Dividing both sides of Equation 9-27 by the influent mass flux, Q_iC_i, gives

$$1 = \frac{Q_eC_e + Q_gC_g}{Q_iC_i} + \frac{Vk_bC_e}{Q_iC_i} \tag{9-28}$$

which can be written as

$$\frac{N}{N_o} = 1 - \frac{Vk_bC_e}{Q_iC_i} \tag{9-29}$$

where N is the sum of the effluent and off-gas mass fluxes and N_o is the mass flux into the reactor in the influent. The ratio N/N_o represents the fraction of the mass flux entering the reactor that leaves the reactor in the effluent and off-gas combined. Solving Equation 9-26 for C_e and substituting it into Equation 9-29 gives

$$\frac{N}{N_o} = 1 - \frac{\bar{t}k_b}{C_i}\left[\frac{C_i}{1+\bar{t}(k_b+k_v)}\right] \tag{9-30}$$

After rearranging and simplifying, Equation 9-30 can be written as

$$\frac{N}{N_o} = \frac{1+\bar{t}k_v}{1+\bar{t}k_v+\bar{t}k_b} \tag{9-31}$$

The ratio N/N_o, was solved as a function of k_b for various values of k_v, and the results are given in Figure 9-7. For a given value of k_b, the ratio N/N_o decreases as the volatility of a compound decreases. The significance of such a plot is that the decrease in N/N_o with increasing values of k_b indicates reductions in both the effluent and off-gases of volatile, biodegradable compounds. As a further illustration, a specific example is given for three different compounds with the following characteristics:

Compound A: non-biodegradable, volatile (k_v = 0.075 min^{-1})

Compound B: biodegradable (k_b=0.0075 min^{-1}), volatile (k_v=0.075 min^{-1})

Compound C: biodegradable (k_b=0.2 min^{-1}), volatile (k_v=0.075 min^{-1})

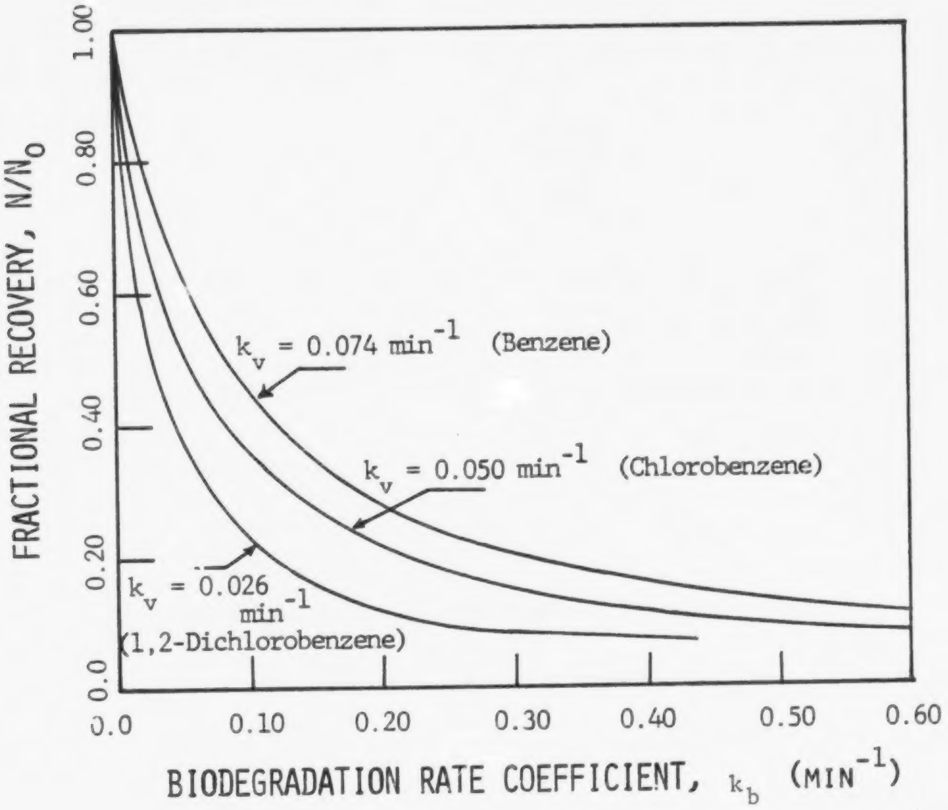


FIGURE 9-7. Effect of increasing volatilization on the disappearance of a compound due to biodegradation by activated sludge in a 10-liter sludge bioreactor.

The effluent concentration can be calculated from Equation 9-32

$$C_e = \frac{C_i}{1+\bar{t}(k_v+k_b)} \tag{9-32}$$

and the off-gas concentration from Equation 9-33

$$C_g = \frac{Vk_vC_e}{Q_g} \tag{9-33}$$

The effluent, off-gas, C_e/C_i and N/N_o values have been calculated for each compound assuming steady-state conditions in the experimental CMF bioreactors with volumes of 10-liters, hydraulic retention times of 5.5 hours, and a total aeration rate of 4 ℓ/min. A comparison of the results in Table 9-1 indicates that increasing the biodegradation rate coefficient resulted in a significant reduction in the off-gas concentration.

TABLE 9-1

PREDICTED FATE OF THREE EXAMPLE COMPOUNDS

Parameter	Compound A	Compound B	Compound C
k_v(min^{-1})	0.075	0.075	0.075
k_b(min^{-1})	0	0.075	0.2
Influent (μg/ℓ)	100	100	100
Effluent (μg/ℓ)	3.8	2.0	1.1
Effluent (% of influent)	3.8	2.0	1.1
C_e/C_i	0.04	0.02	0.01
Off-Gas (μg/ℓ)	0.73	0.37	0.02
Off-Gas (% of influent)	96.2	49.0	27.0
N/N_o	1.0	0.51	0.28
Biodegraded (% of influent)	0	49	72

SECTION 10

RESULTS: CONTROL ACTIVATED SLUDGE BIOREACTOR STUDIES

The fate of each toxic organic compound during activated sludge treatment was studied in the 10-liter bioreactors with activated sludge. The bioreactors were operated in continuous flow modes with influents composed of synthetic wastewater and a toxic organic solution. Influent concentrations of the toxic compounds typically were maintained between 50 and 150 µg/ℓ to simulate concentrations representative of those found in influents to full scale municipal wastewater treatment facilities. Table 10-1 summarizes results from a study of the occurrence of priority pollutants in municipal wastewaters for the compounds used in this project (2).

The activated sludge studies were conducted to fulfill three primary objectives:

1) provide a reference point to which the results from bioreactor studies with PAC could be compared to evaluate the effect of PAC addition on the removal of the toxic organic compounds,

2) determine which of the toxic organic compounds could be biodegraded by activated sludge under conditions representative of municipal activated sludge treatment and,

3) evaluate the relative importance of the three removal mechanisms: volatilization, biodegradation, and biosorption; and model how each affected the fate of the toxic organic compounds during activated sludge treatment.

Previous studies have reported many of the organic priority pollutants to be degraded by activated sludge biomasses (55-59). An extensive review of microbial degradation of organic priority pollutants was reported by Kobayashi and Rittmann (55). Typically biodegradation studies have been conducted in static incubators to minimize volatilization and at concentrations significantly greater than those encountered in municipal wastewaters. Such studies are valuable, but

TABLE 10-1

OCCURRENCE OF ORGANIC PRIORITY POLLUTANTS IN MUNICIPAL WASTEWATERS

	INFLUENT			EFFLUENT		
Compound	Min.	Max.	% Detected[+]	Min.	Max.	% Detected
Toluene	1[++]	13,000	96	1	100	53
Ethylbenzene	1	730	80	1	49	24
Benzene	1	1560	61	1	72	23
Lindane	0.02	3.9	26	0.01	1.40	33
1,2-Dichlorobenzene	1	440	23	1	27	8
Chlorobenzene	1	150	13	1	9	3
1,2,4-Trichlorobenzene	3	4300	10	3	310	4
Nitrobenzene	-	-	ND[+++]	-	-	ND
O-Xylene	-	-	NM[++++]	-	-	NM

[+] Percent of samples in which compound was detected.
[++] Concentrations in μg/ℓ.
[+++] ND = Not Detected
[++++] NM = Not Measured; O-Xylene is not included on the Priority Pollutant List.

their results cannot necessarily be extended to actual treatment conditions. This study evaluated biodegradation in completely-mixed flow, aerated, activated sludge systems by monitoring mass fluxes of individual compounds into and out of the bioreactors.

Biological degradation of a toxic organic compound in the 10-liter experimental bioreactors operated in continuous flow modes was evidenced by a significant difference between the mass fluxes into (influent) and out of (effluent, off-gas and waste sludge combined) the bioreactors. The mass flux of a toxic organic compound into the bioreactors is given by

$$N_o = Q_i \times C_i \qquad (10\text{-}1)$$

and the mass flux out of the bioreactors by

$$N = Q_e C_e + Q_g C_g + C_s Q_s \qquad (10\text{-}2)$$

where Q_i(ℓ/min) is the influent flow rate, Q_e(ℓ/min) is the effluent flow rate, Q_s(ℓ/min) is the waste sludge flow rate, Q_g(ℓ/min) is the off-gas flow rate and is equal to Q_a, the aeration rate, C_i(μg/ℓ) is the influent concentration, C_e(μg/ℓ) is the effluent concentration, C_g(μg/ℓ) is the off-gas concentration and C_s(μg/ℓ) is the concentration in the waste sludge. Background studies conducted in the 10-liter experimental bioreactors without activated sludge demonstrated that measured mass fluxes into and out of the bioreactors were nearly identical for both volatile and non-volatile compounds. Values of N/N_o, the fractional recovery of a toxic compound, averaged between 0.93 to 1.00 when the bioreactors were operated without activated sludge. Therefore, N/N_o values greater than 0.90 were evaluated as complete recovery while values less than 0.9 were interpreted as evidence of biological degradation.

Results from the activated sludge studies conducted in the 10-liter CMF bioreactors with single toxic solutes showed significant biodegradation of benzene, toluene, ethylbenzene, o-xylene, chlorobenzene and nitrobenzene. Lindane and 1,2,4-trichlorobenzene were found to be non-biodegradable while 1,2-dichlorobenzene was poorly biodegraded. Table 10-2 summarizes the fate of each compound during activated sludge treatment in experimental bioreactors operated at 6-day SRT's under steady-state conditions.

10.1 ACTIVATED SLUDGE BIOREACTOR OPERATING CONDITIONS

All activated sludge studies were begun by filling the bioreactors with activated sludge from the aeration basin of the Ann Arbor wastewater treatment facility. The bioreactors were operated in continuous flow modes for at least two weeks to acclimate the microorganisms to the synthetic wastewater prior to adding the toxic organics to the influent. A summary of the pertinent operating conditions used during the activated sludge bioreactor studies is reported in Table 10-3.

TABLE 10-2

FATE OF TOXIC ORGANICS IN ACCLIMATED ACTIVATED SLUDGE BIOREACTORS OPERATED AT 6-DAY SRT'S UNDER STEADY-STATE CONDITIONS

	Percent of Influent			
Compound	Effluent	Off-Gas	Biosorbed	Biodegraded*
Benzene	<1	16	0	84
Toluene	<1	17	0	83
Ethylbenzene	<1	22	0	78
O-Xylene	<1	25	0	75
Chlorobenzene	<1	20	0	80
1,2-Dichlorobenzene	6	59	0	35
1,2,4-Trichlorobenzene	10	90	<1	0
Nitrobenzene	2	<1	0	98
Lindane	95	0	5	0

*Calculated

MLSS = 3200 - 3800 mg/ℓ
$\bar{t}$ = 5.5 - 6.0 hours
Q_a = 3.8 - 4.2 ℓ/min
Q_s = 1.67 ℓ/day

TABLE 10-3

BIOREACTOR OPERATING CONDITIONS USED DURING ACTIVATED SLUDGE STUDIES

Influent flow	28-30 mℓ/min
Hydraulic retention time	5.5-6.0 hrs.
Aeration rate	3.8-4.2 ℓ/min
Influent soluble TOC	90-110 mg/ℓ
Effluent soluble TOC	10-20 mg/ℓ
Solids retention time (SRT)	3-12 days
MLSS (3-day SRT)	1700-2100 mg/ℓ
MLSS (6-day SRT)	3200-3800 mg/ℓ
MLSS (12-day SRT)	6800-7500 mg/ℓ
pH	7.0-7.2

10.2 SYSTEM PERFORMANCE WITH RESPECT TO TOC REMOVAL

While the primary focus of the project was the removal of specific organic compounds, data was collected on overall organics removal as measured by soluble total organic carbon (TOC). The decision to use TOC as the indicator of system performance with respect to overall organics removal was based on the need to process large numbers of samples. Analytical procedures for the toxic compounds were time consuming and precluded the use of the more lengthy BOD or COD analyses. Influent and effluent TOC samples were typically conducted every two to four days during steady-state operating conditions and more frequently during non-steady-state periods.

The removal of soluble TOC typically ranged from 80 to 90% for all bioreactor studies. Average TOC removals were not dependent upon the solids retention time between 3 and 12-days as shown by results from bioreactor studies conducted at 3, 6, and 12-day SRT's in Figures 10-1 through 10-5. A summary of average influent, effluent and percent removals for each control activated sludge bioreactor study presented in Figures 10-1 through 10-5 is given in Table 10-4. The average TOC removal of 86% for those studies was the same as the overall TOC removal averaged from all of the steady-state control activated sludge studies.

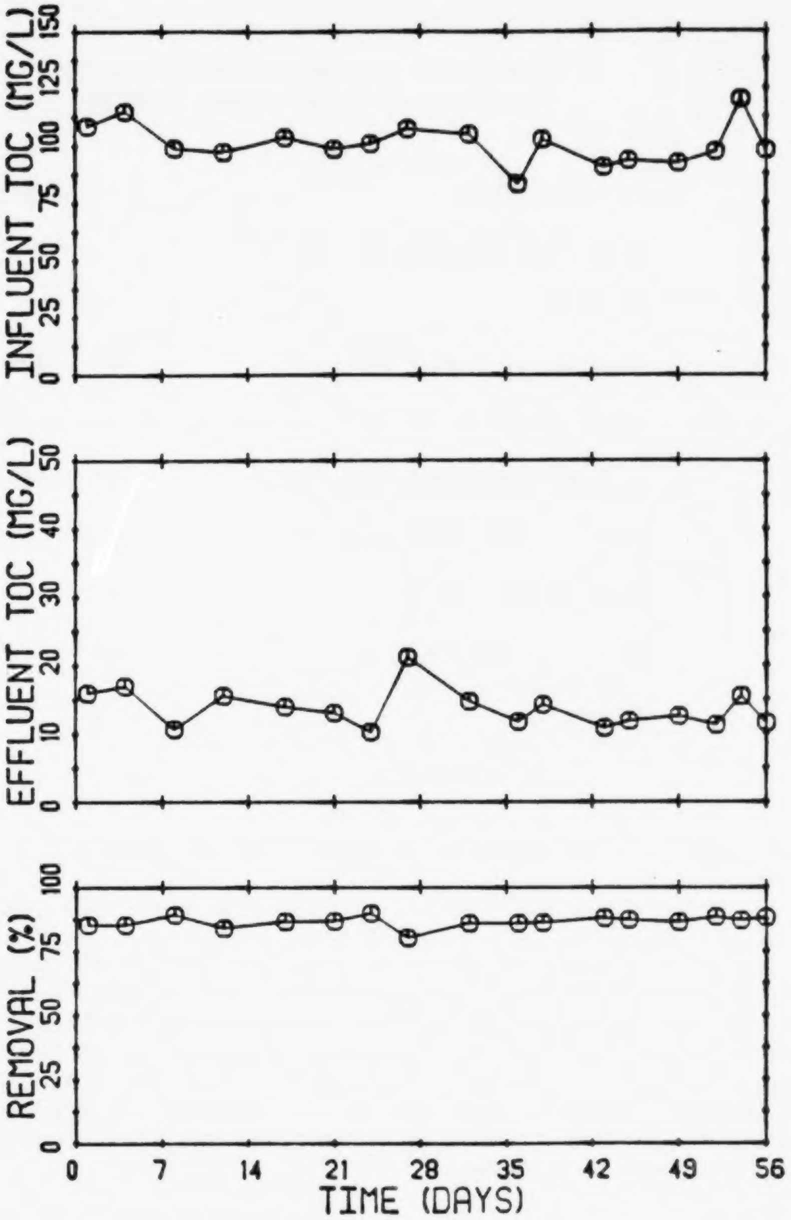


FIGURE 10-1. Soluble TOC removal in a 10-liter activated sludge bioreactor operated with a 3-day SRT.

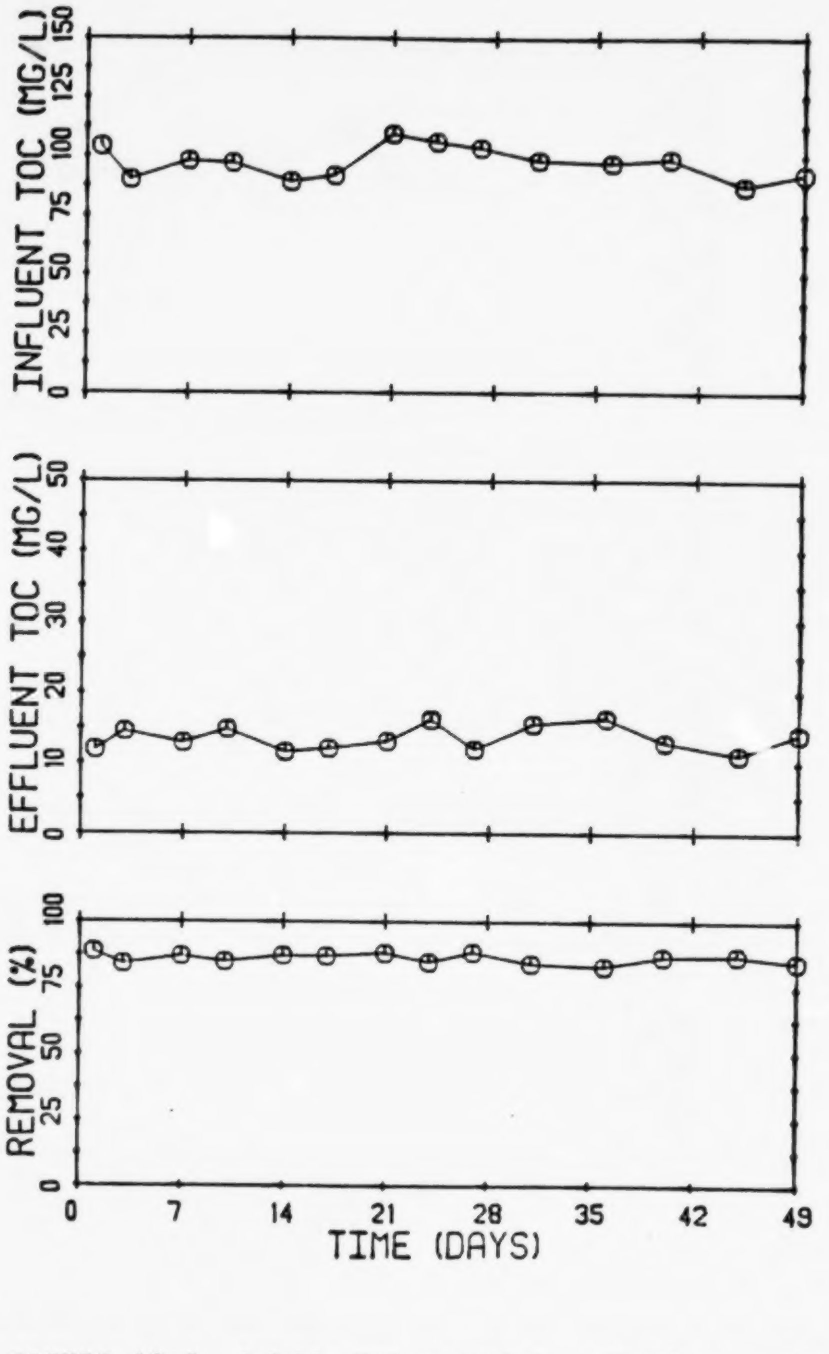


FIGURE 10-2 Soluble TOC removal in a 10-liter activated sludge bioreactor operated with a 6-day SRT.

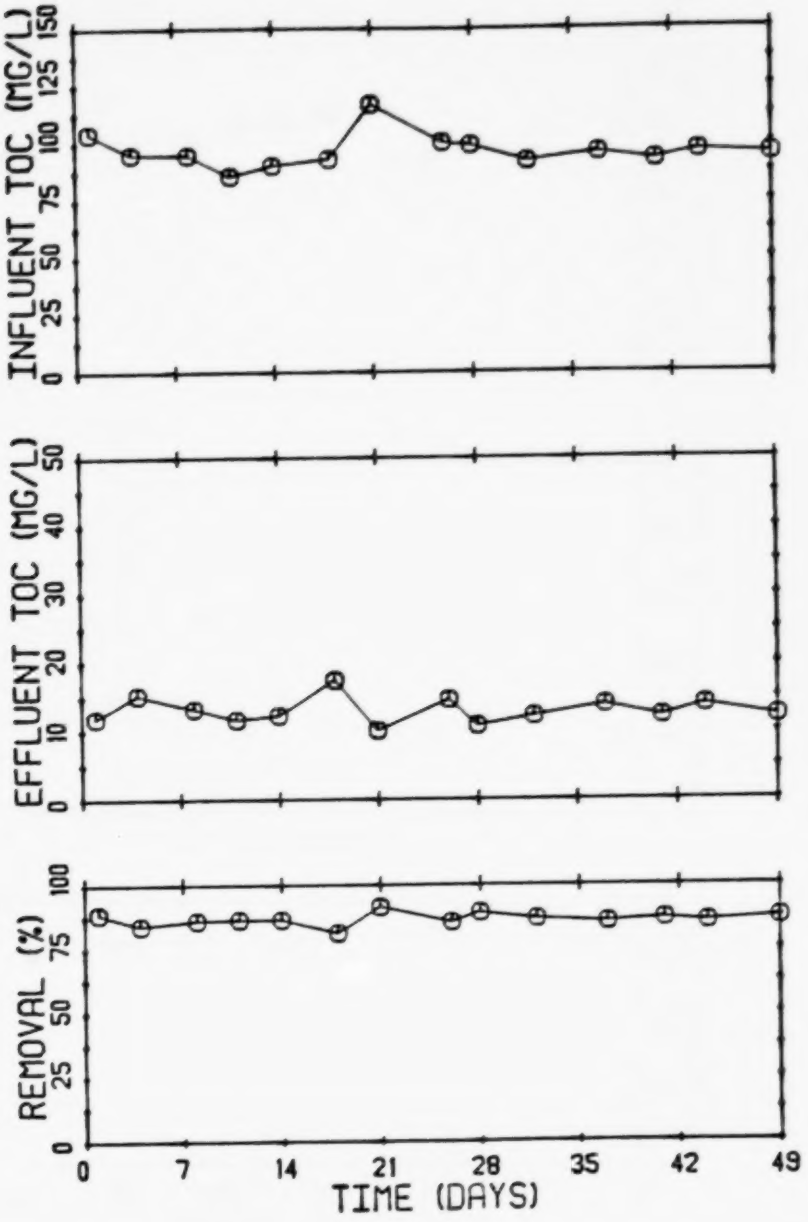


FIGURE 10-3. Soluble TOC removal in a 10-liter activated sludge bioreactor operated with a 6-day SRT.

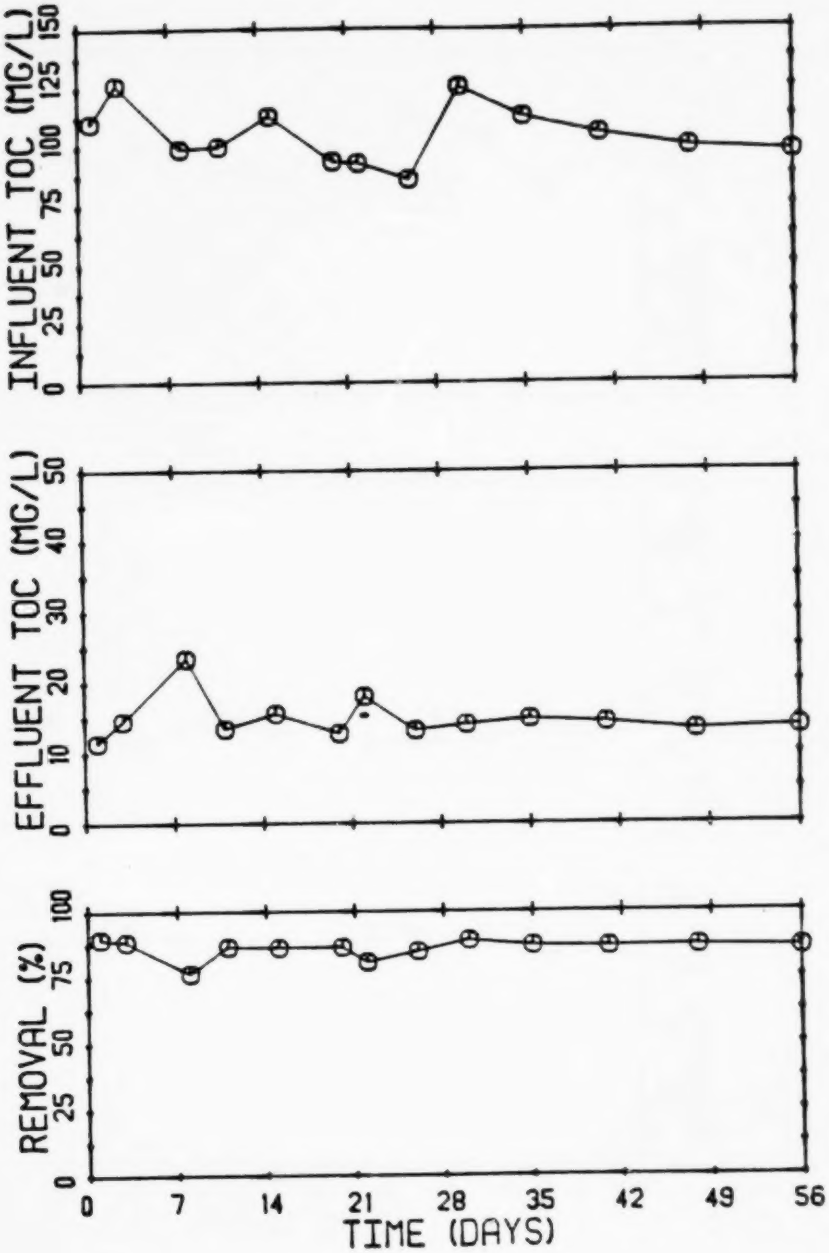


FIGURE 10-4. Soluble TOC removal in a 10-liter activated sludge bioreactor operated with a 6-day SRT.

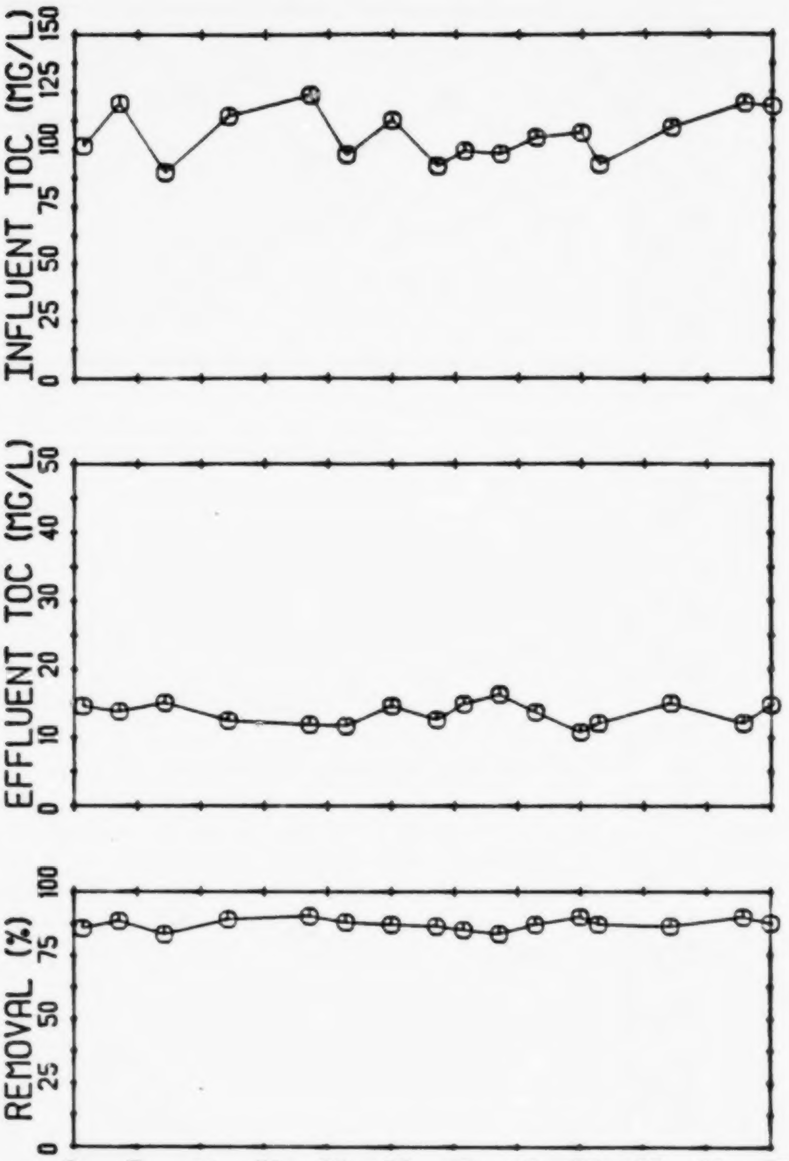


FIGURE 10-5. Soluble TOC removal in a 10-liter activated sludge bioreactor operated with a 12-day SRT.

No correlation between TOC removal and the removal of an individual toxic compound existed for data collected during activated sludge bioreactor studies with influent toxics in the concentration range typical of municipal wastewaters, 0 to 1000 μg/ℓ. There was evidence that shock loadings of nitrobenzene sufficient to cause an inhibition of nitrobenzene degradation also resulted in periods of reduced TOC removal. A more complete analysis of these findings will be included in a discussion of the effect of high influent toxics concentrations. In bioreactor studies with influent toxic concentrations in the 50 to 150 μg/ℓ range no change in overall TOC removal was observed during periods immediately following the initial addition of a toxic organic to the influent.

TABLE 10-4

SUMMARY OF TYPICAL MEAN INFLUENT AND EFFLUENT SOLUBLE TOC CONCENTRATIONS AND PERCENT REMOVALS FROM BIOREACTOR STUDIES OPERATED AT 3,6,9, AND 12-DAY SRT's

Solids Retention Time (days)	Influent TOC (mg/ℓ)	Effluent TOC (mg/ℓ)	TOC Removal (%)
3	100.8 (8.9)+	13.7 (2.8)	86.2 (2.2)
3	105.6 (10.2)	14.7 (2.3)	85.9 (2.6)
6	97.8 (6.7)	13.5 (1.8)	86.1 (1.8)
6	96.5 (7.3)	12.9 (1.8)	86.4 (2.4)
6	107.1 (8.1)	14.7 (2.9)	86.3 (2.7)
6	102.6 (8.4)	14.6 (2.0)	85.8 (2.0)
9	104.7 (12.2)	14.8 (3.0)	86.7 (3.5)
9	101.9 (8.4)	14.4 (2.1)	85.7 (2.5)
12	106.3 (13.5)	13.5 (1.6)	87.1 (2.2)
All Single Solute Activated Sludge Studies	103.2 (10.2)	14.1 (2.2)	86.3 (2.4)

+ Values in parenthesis are the standard deviation

Completely-mixed batch TOC biodegradation rate studies were conducted in two different reactors; the 2.6 liter glass CMB reactors and the 10-liter experimental bioreactors operated in batch modes by temporarily stopping the influent and sludge waste flows. Biodegradation rate coefficients for TOC removal measured in the 2.6-liter CMB reactor and 10-liter bioreactor with the same activated sludge (6-day SRT) were nearly identical. A comparison of the results from two such studies is presented in Figure 10-6.

The biodegradation rate coefficient in each case was 0.016 min^{-1}. Subsequent measurements of TOC biodegradation rate coefficients were made in the 10-liter experimental bioreactors temporarily operated in batch modes. The average biodegradation rate coefficient measured in bioreactors operated at 6-day SRT's was 0.016 min^{-1}.

TOC biodegradation rate studies were also conducted with mixed liquor from 12-day SRT bioreactors. The average biodegradation rate coefficient for the 12-day SRT activated sludges was 0.018 min^{-1}. A comparison of typical results from TOC biodegradation rate studies using activated sludges from 6 and 12-day SRT bioreactors is given in Figure 10-7.

10.3 FATE OF NON-BIODEGRADABLE AND POORLY BIODEGRADABLE ORGANIC COMPOUNDS

10.3.1. Non-volatile Compound

Activated sludge bioreactor studies showed lindane to be a non-volatile, non-biodegradable compound in the experimental system. A small amount of lindane was biosorbed by the activated sludge resulting in effluent concentrations slightly lower than the influent concentrations. Results from activated sludge studies conducted in bioreactors operated at 3, 6, and 9-day solids retention times are presented in Figures 10-8, 10-9, and 10-10, respectively. Each figure presents influent and effluent concentrations and C/C_i values, the ratio of effluent to influent concentrations. Off-gas samples were not collected because results from baseline CMF bioreactor studies conducted without activated sludge demonstrated lindane was non-volatile. A summary of results from the lindane activated sludge studies is given in Table 10-5. The reduction in the aqueous lindane concentration in bioreactors with 6 and 9-day SRT's was the same and averaged about 8%. Slightly less removal, approximately 5%, was observed in the bioreactor with the 3-day solids retention time. Near complete recoveries of lindane were obtained from each bioreactor when waste mixed liquor suspended solids were extracted with an organic solvent and the concentration of lindane was measured.

Removal of a non-volatile, non-biodegradable compound during activated sludge treatment can be modeled by Equation 9-16 developed in

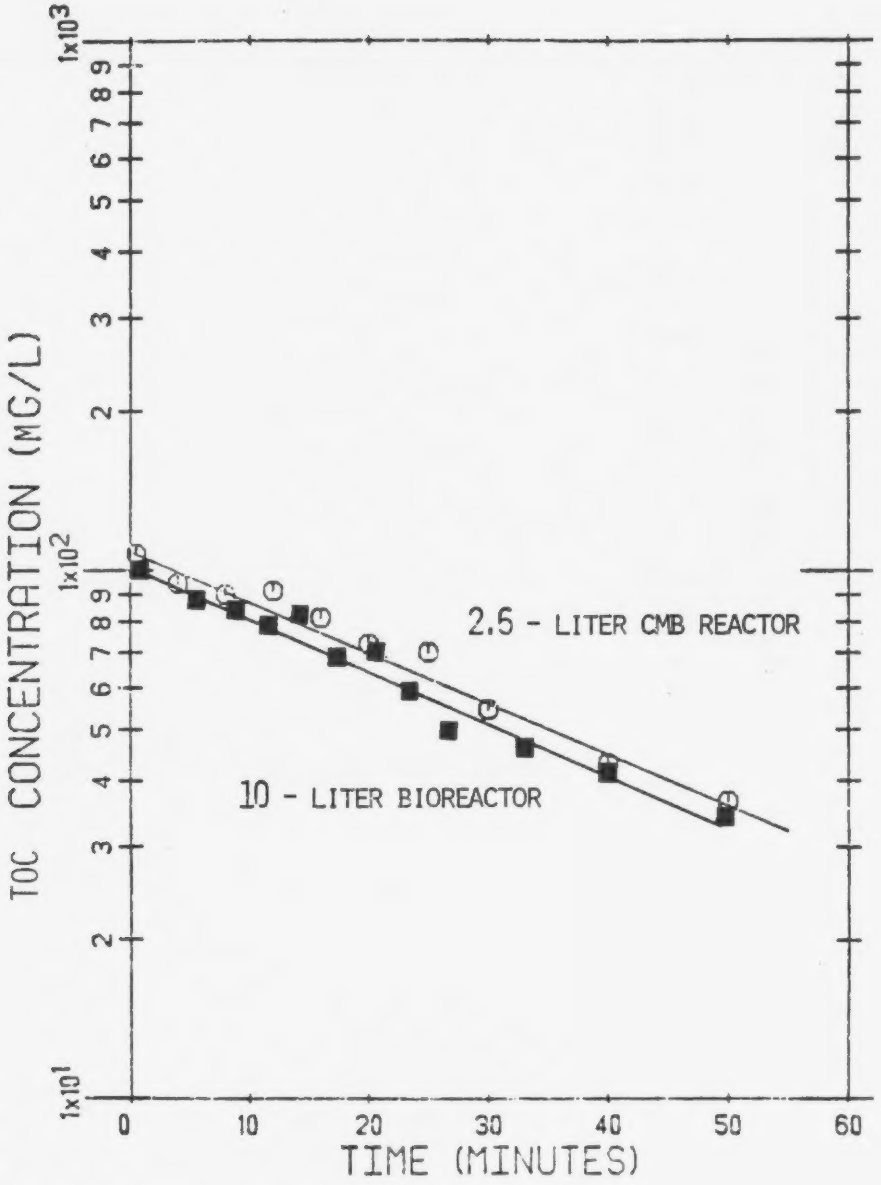


FIGURE 10-6. Comparison of results from soluble TOC degradation rate studies in 2.6-liter and 10-liter experimental bioreactors with activated sludge.

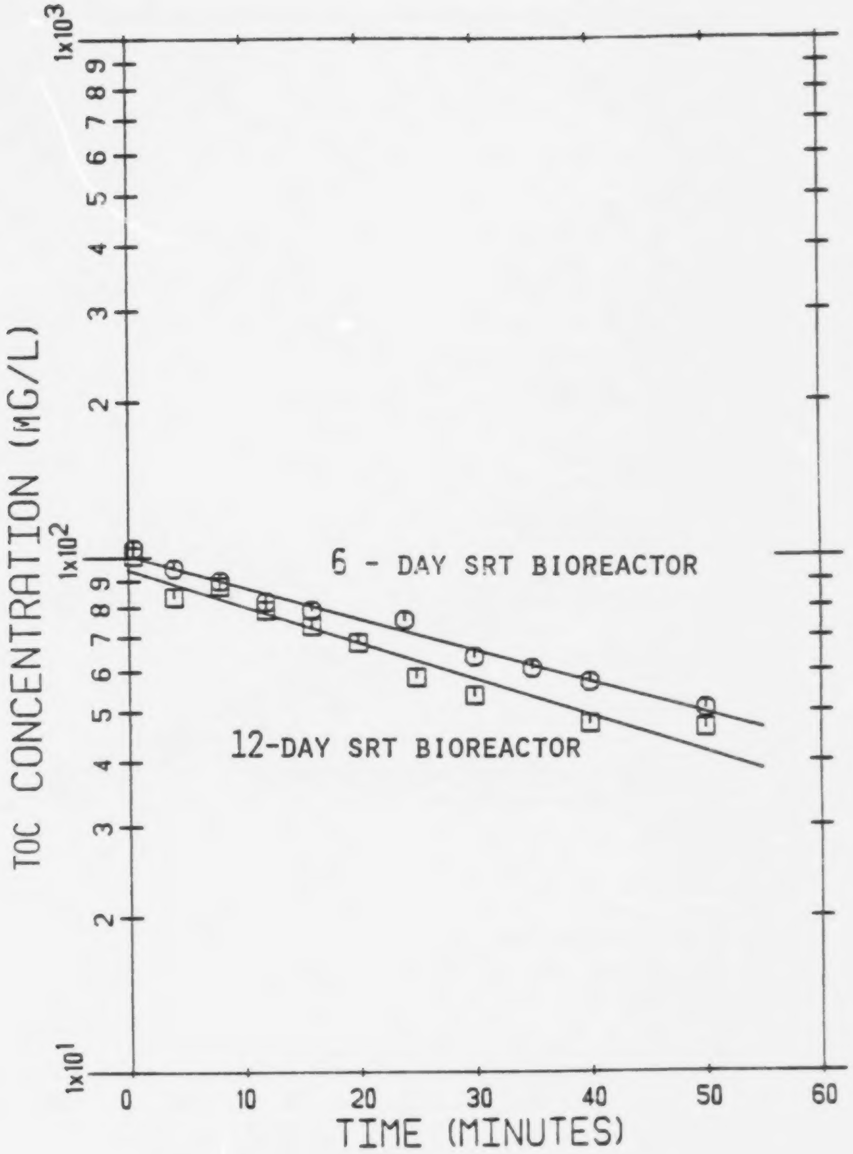


FIGURE 10-7. Comparison of results from soluble TOC degradation rate studies conducted in 10-liter activated sludge bioreactors operated with 6 and 12-day SRT's.

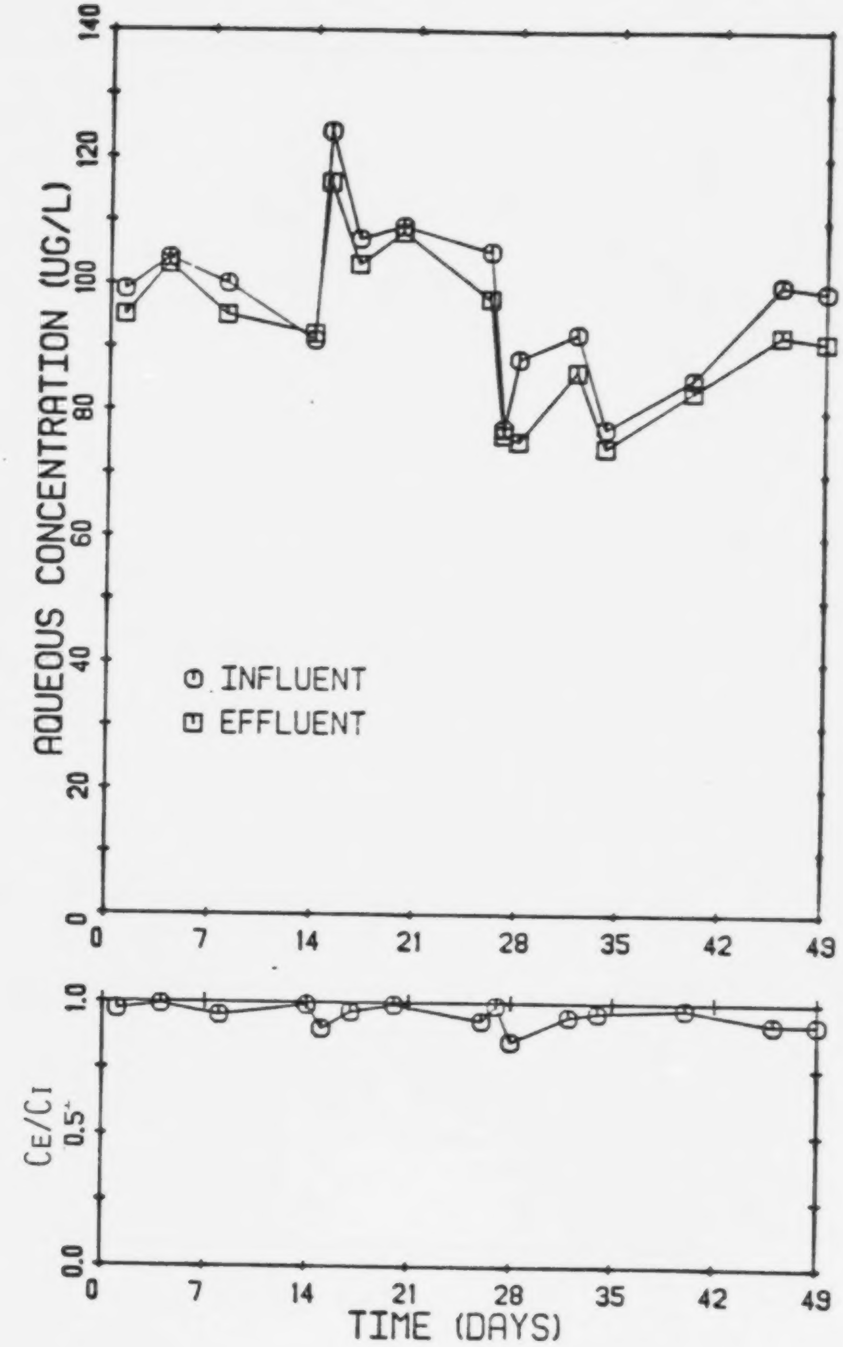


FIGURE 10-8. Lindane results from a 10-liter activated sludge bioreactor study conducted with a 3-day SRT.

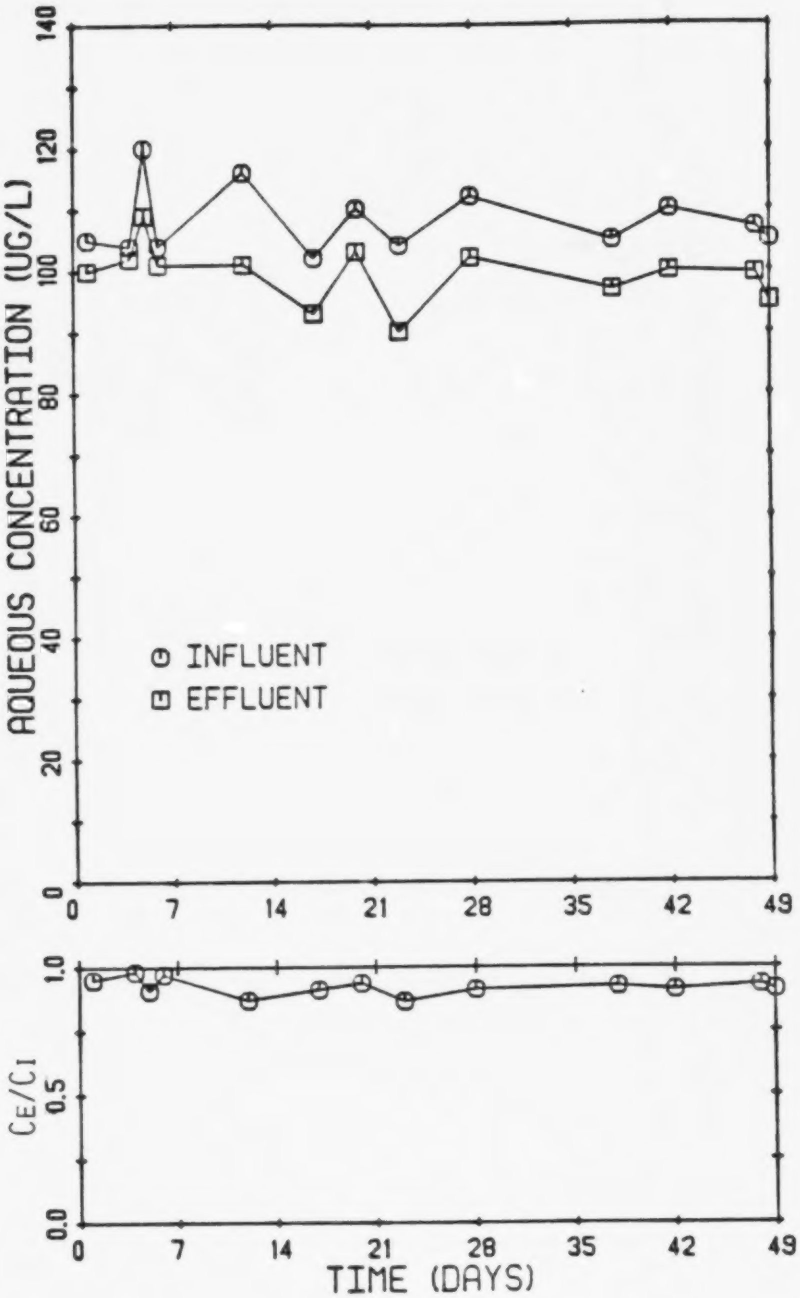


FIGURE 10-9. Lindane results from a 10-liter activated sludge bioreactor study conducted with a 6-day SRT.

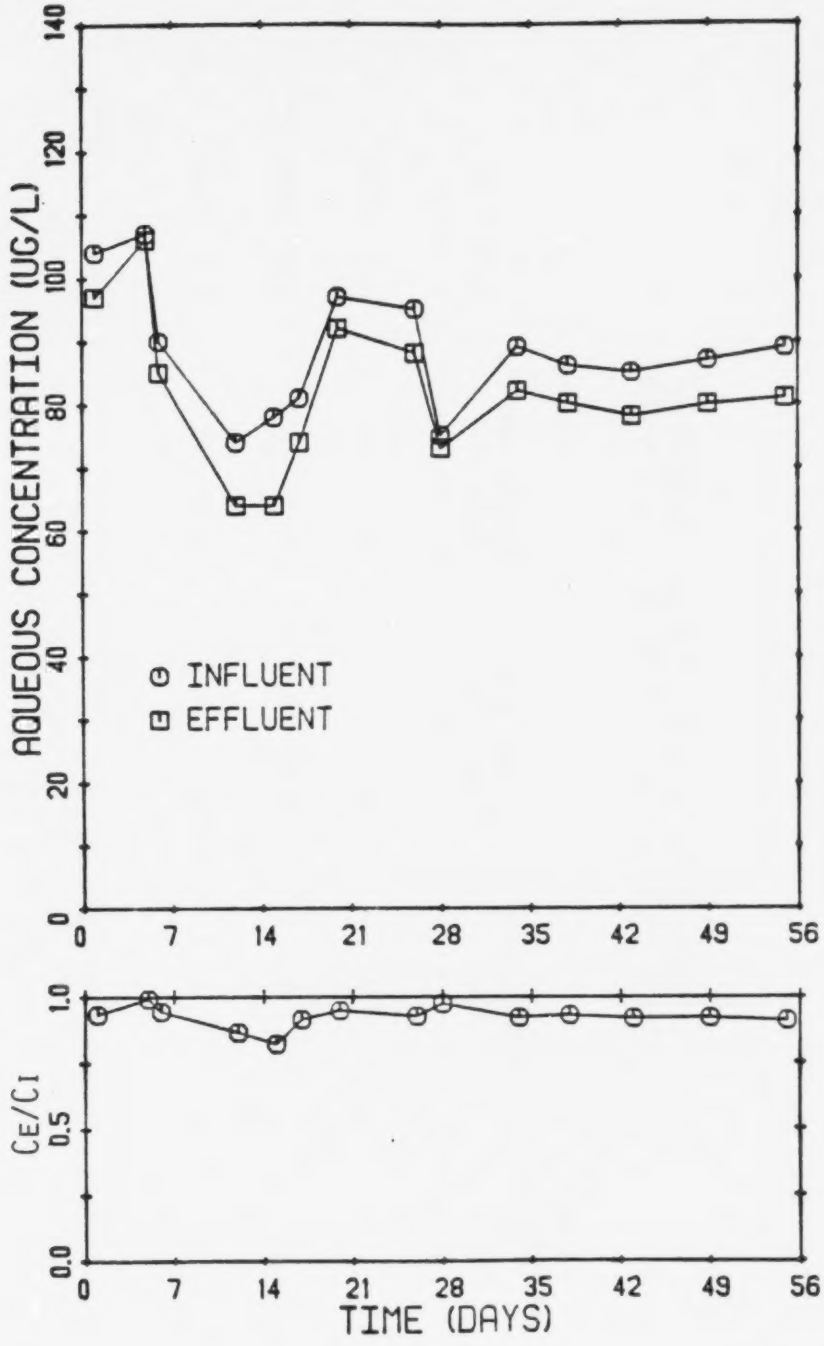


FIGURE 10-10. Lindane results from a 10-liter activated sludge bioreactor study conducted with a 9-day SRT.

TABLE 10-5

LINDANE REMOVAL IN ACTIVATED SLUDGE BIOREACTORS
OPERATED WITH 3,6, and 9-DAY SOLIDS RETENTION TIMES

Solids Retention Time (days)	MLSS (mg/ℓ)	INFLUENT (μg/ℓ)		EFFLUENT (μg/ℓ)		C_e/C_i	
	Mean	Mean	S.D.	Mean	S.D.	Mean	S.D.
3	1600	97.5	13.5	92.5	12.3	0.95	0.04
6	3300	108.0	5.2	99.4	4.8	0.92	0.03
9	4500	88.4	9.9	81.7	11.6	0.92	0.04

S.D. Standard Deviation

Section 9. The value of K_B from the equilibrium sorption study was incorporated into Equation 9-16 along with values for the appropriate bioreactor operating parameters to predict the effluent lindane concentrations from the 3, 6, and 9-day SRT activated sludge units. Concentrations of MLSS used in the model were those reported in Table 10-5, and the hydraulic retention time was 5.5 hours. Comparisons of measured and predicted effluent concentrations and C_e/C_i values for lindane activated sludge studies conducted in bioreactors operated at 3, 6, and 9-day SRT's given in Table 10-6 show that there was good agreement between predicted and measured values.

TABLE 10-6

COMPARISON OF MEASURED AND PREDICTED
RESULTS FROM LINDANE ACTIVATED SLUDGE STUDIES

SRT (days)	Influent (µg/ℓ)	Effluent (µg/ℓ)		C_e/C_i	
		Measured	Predicted	Measured	Predicted
3	97.5	92.5	91.2	0.95	0.94
6	108.0	99.4	99.8	0.92	0.92
9	88.4	81.7	83.0	0.92	0.94

10.3.2. Volatile Compounds

10.3.2.1. 1,2,4-Trichlorobenzene

Activated sludge studies with 1,2,4-trichlorobenzene were conducted in bioreactors operated with 6 and 12-day solids retention times. Results from these studies demonstrated that 1,2,4-trichlorobenzene was a volatile non-biodegradable compound in the experimental activated sludge system. Influent, effluent, and off-gas concentrations recorded during the two studies are plotted in Figure 10-11 along with N/N_0 values representing the fractional recovery of 1,2,4-trichlorobenzene.

Results from the 6 and 12-day SRT activated sludge studies were not significantly different. Effluent and off-gas concentrations during the 6-day SRT study averaged 12.0 µg/ℓ and 706 ng/ℓ, respectively, for a mean influent concentration of 116.6 µg/ℓ. The slightly lower influent concentration during the 12-day SRT study, 101.5 µg/ℓ, resulted in average effluent and off-gas concentrations of 10.2 µg/ℓ and 622 ng/ℓ.

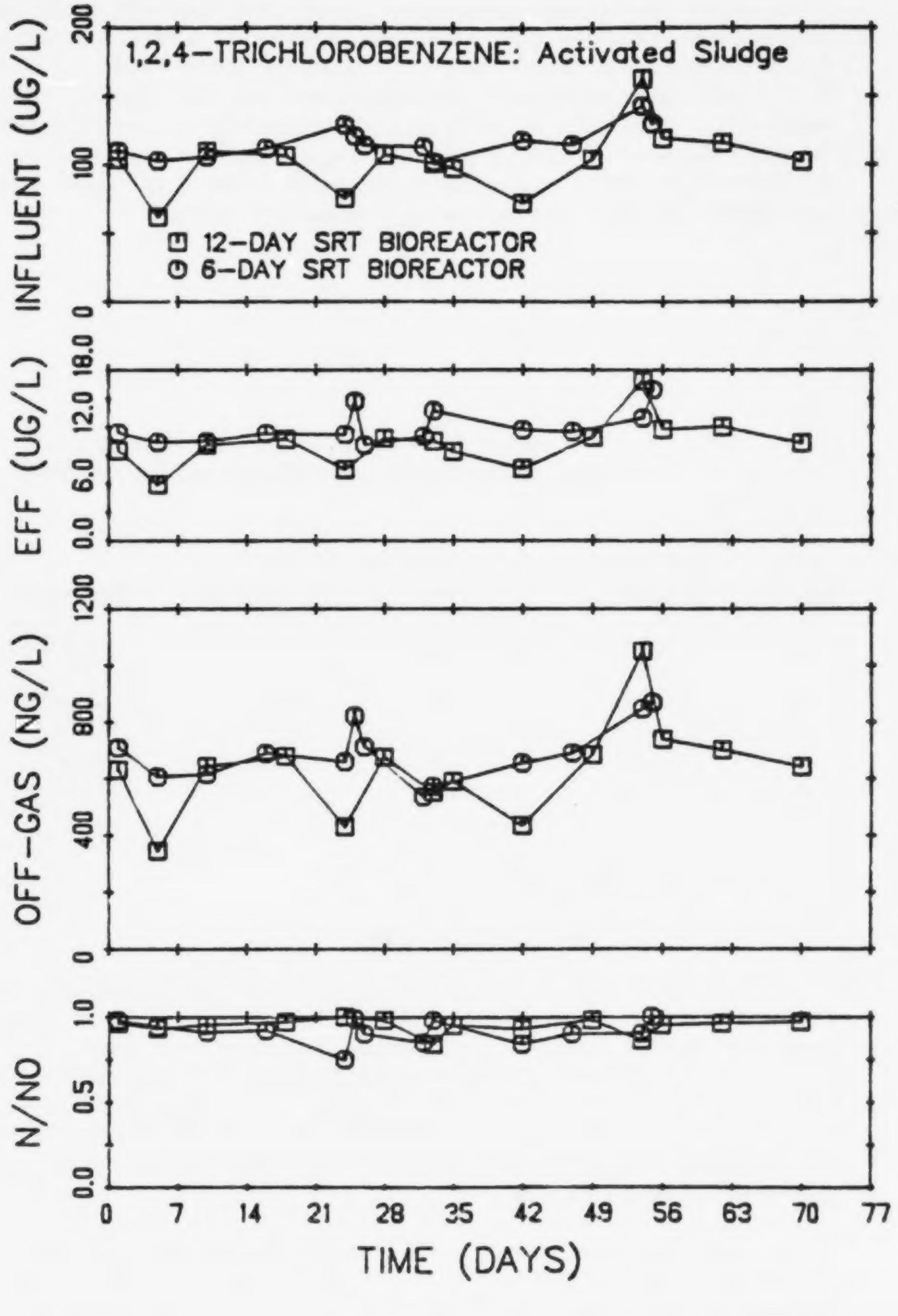


FIGURE 10-11. 1,2,4-Trichlorobenzene results from activated sludge studies conducted in 10-liter bioreactors operated with 6 and 12-day SRT's.

TABLE 10-7

COMPARISON OF MEASURED AND PREDICTED EFFLUENT AND OFF-GAS 1,2,4-TRICHLOROBENZENE CONCENTRATIONS FROM ACTIVATED SLUDGE BIOREACTORS

	Influent (μg/ℓ)	Effluent (μg/ℓ)	Off-Gas (ng/ℓ)	N/N_o
	6-DAY SRT BIOREACTOR			
Measured	116.6 (11.8)+	12.0 (1.8)	706 (112)	0.93 (0.05)
Predicted if no Biodegradation	--	12.3 (1.5)	772 (95)	1.00 (0.0)
Predicted from Effluent	--	--	754 (115)	0.99 (0.16)
	12-DAY SRT BIOREACTOR			
Measured	101.5 (27.7)	10.2 (2.7)	622 (181)	0.94 (0.05)
Predicted if no Biodegradation	--	10.5 (3.2)	662 (204)	1.00 (0.0)
Predicted from Effluent	--	--	646 (173)	0.98 (0.06)

+ ( ) Standard Deviation

In both studies the amount of 1,2,4-trichlorobenzene in the effluent represented only 10% of the total amount entering the bioreactors. The remaining 1,2,4-trichlorobenzene was stripped from solution and exited the units in the off-gas. Recoveries of 1,2,4-trichlorobenzene averaged 93 and 94%, respectively, in the 6-day and 12-day SRT bioreactors. The recovery of 1,2,4-trichlorobenzene during baseline studies conducted in the 10-liter bioreactors without activated sludge averaged approximately 94%. The results from the activated sludge studies indicated that within experimental error complete recoveries of 1,2,4-trichlorobenzene occurred. Influent, effluent, and off-gas concentrations and N/N_o values measured during the two studies are recorded in Table 10-7. The fate of 1,2,4-trichlorobenzene observed in the experimental activated sludge system is summarized by Table 10-8.

TABLE 10-8

FATE OF 1,2,4-TRICHLOROBENZENE IN 6-AND 12-DAY SRT ACTIVATED SLUDGE STUDIES

	Percent of Influent Flux	
	6-Day SRT	12-Day SRT
Effluent	10.3	10.0
Off-Gas	89.2	89.5
Biodegraded	0	0
Biosorbed	<0.5	<0.5

The use of off-gas analyses to facilitate a mass balance for the volatile compounds was an important and unique contribution of this work. Data from the 6-day SRT study has been plotted in Figure 10-12 without the measured amounts of 1,2,4-trichlorobenzene stripped to the atmosphere. The value of C_e/C_i which represents the effluent to influent concentration ratio indicates only that an approximate 90% reduction in the aqueous concentration of 1,2,4-trichlorobenzene occurred. The information in Figure 10-12 does not provide insight into the fate of the 90% of the 1,2,4-trichlorobenzene that disappeared from the aqueous phase. Amounts of the volatile compounds stripped to the atmosphere were not considered as removed, nor should they be in actual treatment systems since this constitutes a redistribution of the compounds in the environment.

While overall recoveries of both lindane and 1,2,4-trichlorobenzene exceeded 90% in the experimental system, effluent concentrations of the two compounds were significantly different. Effluent lindane concentrations were approximately equal to influent concentrations whereas effluent 1,2,4-trichlorobenzene concentrations averaged only 10% of the influent concentrations.

The air-stripping model developed in Section 9-3 was used to predict the effluent and off-gas concentrations of

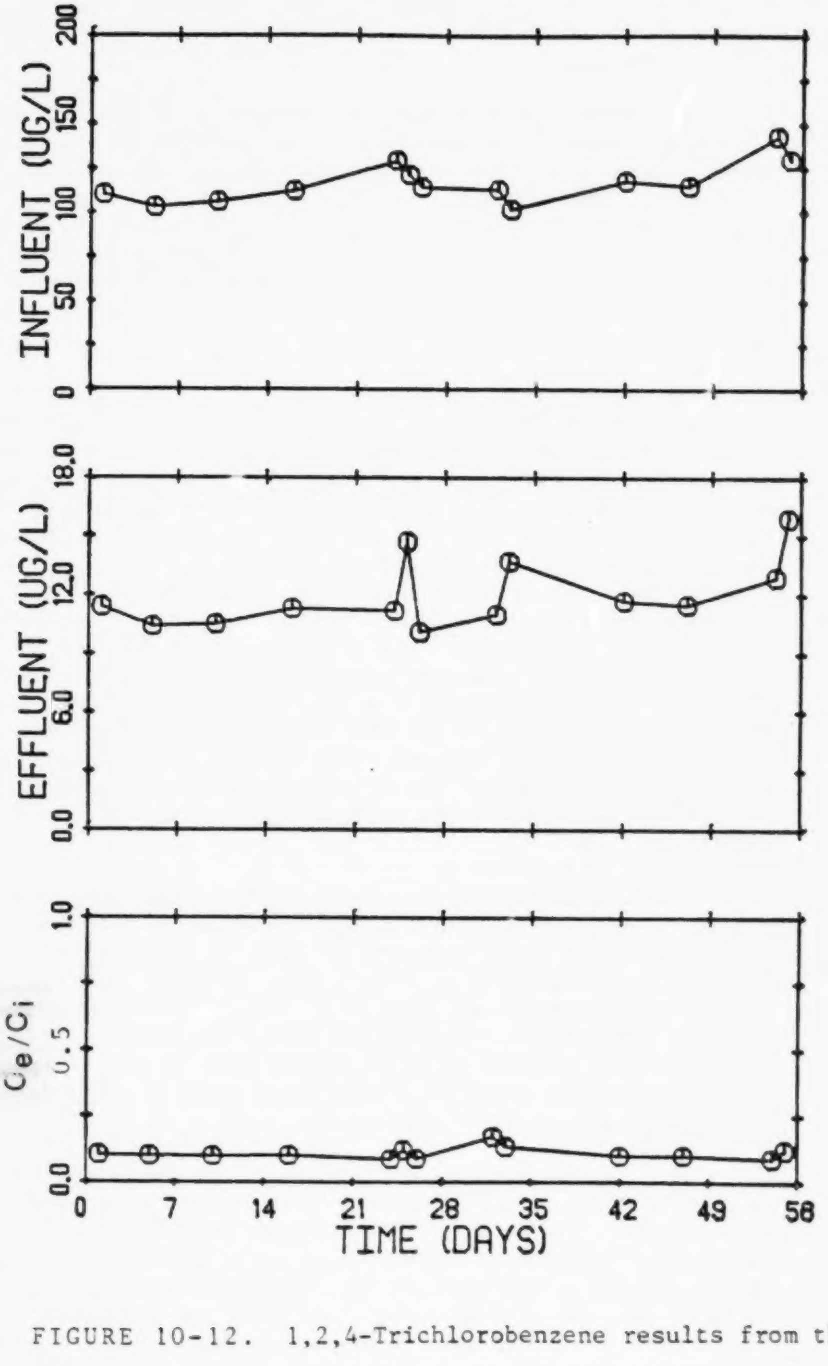


FIGURE 10-12. 1,2,4-Trichlorobenzene results from the 6-day SRT activated sludge study plotted without off-gas concentration data.

1,2,4-trichlorobenzene. Equations 9-11 and 9-12 were used to calculate effluent and off-gas concentrations from measured influent concentrations, influent flow rates, and aeration rates. Predicted effluent and off-gas concentrations, for the 6-day SRT study plotted as dashed lines in Figure 10-13, showed good agreement with the measured data points.

A summary of measured and predicted values for the activated sludge bioreactors operated at 6 and 12-day SRT's is given in Table 10-7. Predicted and measured effluent concentrations averaged 12.3 and 12.0 µg/ℓ, respectively, during the 6-day SRT study. The ability of the air stripping model to successfully predict effluent and off-gas 1,2,4-trichlorobenzene concentration suggests that the biological solids in the mixed liquor had little effect on air-stripping since the volatilization rate parameters were developed from batch experiments without activated sludge.

The model used to generate the predicted values in Figure 10-13 did not include a sorption term. While results from batch equilibrium studies indicated a significant sorption of 1,2,4-trichlorobenzene can occur, biosorption must be considered in relation to other removal mechanisms such as volatilization. Figure 9-5 showed that the effect of biosorption on the ratio of influent to effluent concentration decreased as the volatility of a compound increased. Results given by Figure 9-5 suggest that the effluent and off-gas concentrations of 1,2,4-trichlorobenzene should not be significantly affected by the inclusion of a sorption term in the model. Effluent and off-gas concentrations of 1,2,4-trichlorobenzene predicted by the removal model which included volatilization and sorption were the same as presented in Figure 10-13 for the 6-day SRT bioreactor. There were no significant differences between effluent and off-gas concentrations predicted with and without including a biosorption term in the toxics removal model for 1,2,4-trichlorobenzene because air-stripping was the dominant mechanism.

Concentrations of 1,2,4-trichlorobenzene measured in the waste sludge from the 6-day SRT unit by extracting the mixed liquor suspended solids averaged approximately 40 µg/ℓ or four times greater than the effluent concentrations. Therefore, although sorption of 1,2,4-trichlorobenzene onto the biomass did not significantly affect the effluent concentrations, it did result in concentrations in the sludge significantly greater than in the aqueous phase. Settling and thickening of biological solids would produce significantly larger concentrations in secondary sludges.

The unique feature of this work was the off-gas analyses that enabled formulation of complete mass balances and determination of the fate of each compound. While off-gas sampling was possible under controlled laboratory conditions, it is generally not feasible at full scale treatment facilities. An important finding of this work was that off-gas concentrations could accurately be predicted from measured effluent concentrations. Measured influent and effluent concentrations

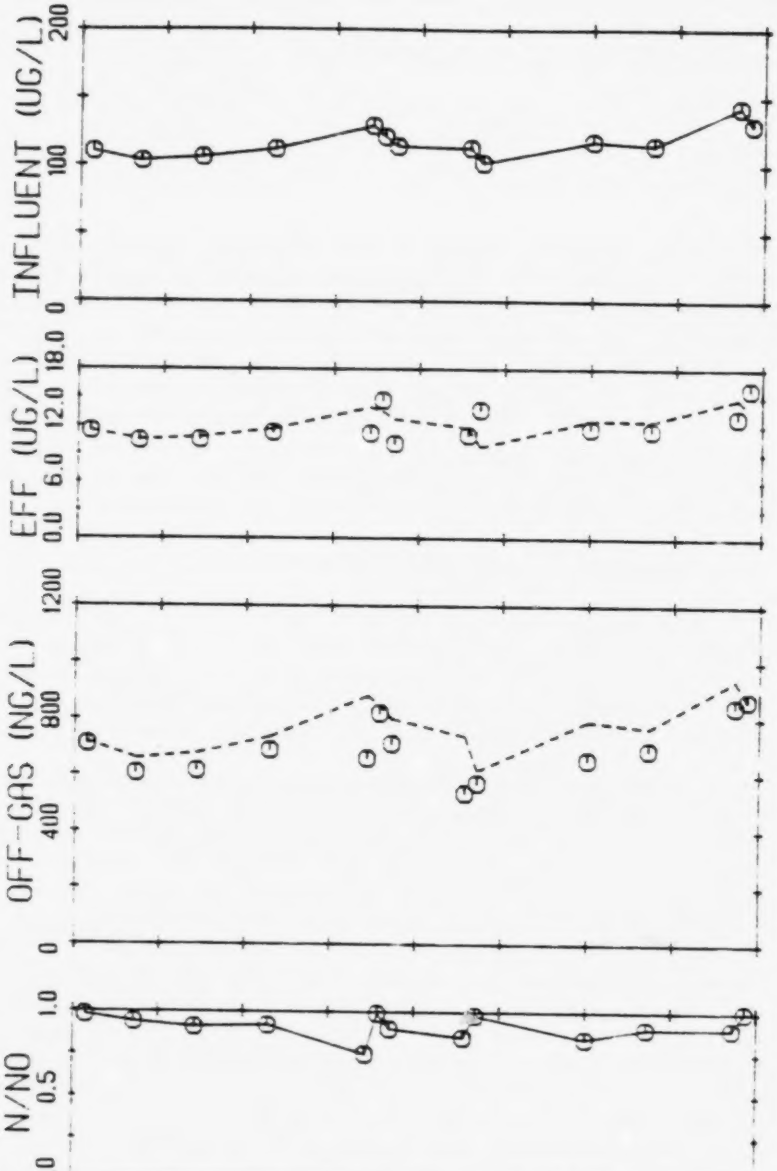


FIGURE 10-13. 1,2,4-Trichlorobenzene effluent and off-gas concentrations predicted by the air-stripping model for the case of no biodegradation in the 10-liter activated sludge bioreactors.

were combined with predicted off-gas concentrations to determine N/N_o values of a volatile compound. Off-gas concentrations from the experimental bioreactors were predicted by substituting the equivalent value of Q_a for Q_g in Equation 7-8:

$$C_g = \frac{VC_e(Q_a L + k_{v,o})}{Q_a} \qquad (10\text{-}3)$$

Predicted off-gas concentrations and N/N_o values, represented by dashed lines, are compared with measured values in Figure 10-14 for the 6-day SRT activated sludge bioreactor. The results, summarized in Table 10-7, show that the effluent concentrations could be used to accurately quantify the amount of a volatile compound stripped to the air. The ability of the model to predict off-gas concentrations was dependent upon the accuracy with which effluent concentrations could be measured. A comparison of Figures 10-13 and 10-14 indicates that either the influent or effluent concentration can be used to predict the off-gas concentration.

10.3.2.2. 1,2-Dichlorobenzene

Batch air-stripping studies conducted in the 10-liter bioreactors demonstrated that the volatilities of 1,2,4-trichlorobenzene and 1,2-dichlorobenzene were nearly identical. Equilibrium sorption studies indicated that the amount of 1,2-dichlorobenzene sorbed by the activated sludge was considerably smaller than the amount of 1,2,4-trichlorobenzene.

Activated sludge studies with 1,2-dichlorobenzene were conducted in 10-liter CMF bioreactors operated at solids retention times of 6 and 12 days. Results from the two studies presented in Figure 10-15 include measured influent, effluent, and off-gas concentrations and N/N_o values representing the fractional recoveries of 1,2-dichlorobenzene. Results from the 6-day SRT study have been replotted in Figure 10-16 with effluent and off-gas concentrations predicted by the air stripping model to occur if volatilization was the only removal mechanism operative in the system. The model generated values depicted by dashed lines represent the steady-state partitioning of 1,2-dichlorobenzene between aqueous and gaseous phases for the operating conditions used in this particular bioreactor study. A mass balance with the predicted effluent and off-gas concentrations would give a complete recovery of 1,2-dichlorobenzene. Including a biosorption term in the model had no effect upon the predicted concentrations of 1,2-dichlorobenzene in the effluent and off-gas. Extractions performed on the waste activated sludge failed to yield concentrations in excess of the aqueous concentration.

Unlike the results for 1,2,4-trichlorobenzene, there was a significant difference between measured effluent and off-gas concentrations and those concentrations predicted by the air-stripping model which assumes only volatilization effects a reduction in the aqueous concentration. The fact that the measured concentrations were less than the predicted ones resulted in N/N_o values less than 0.90. The incomplete recovery indicated that another removal mechanism was producing

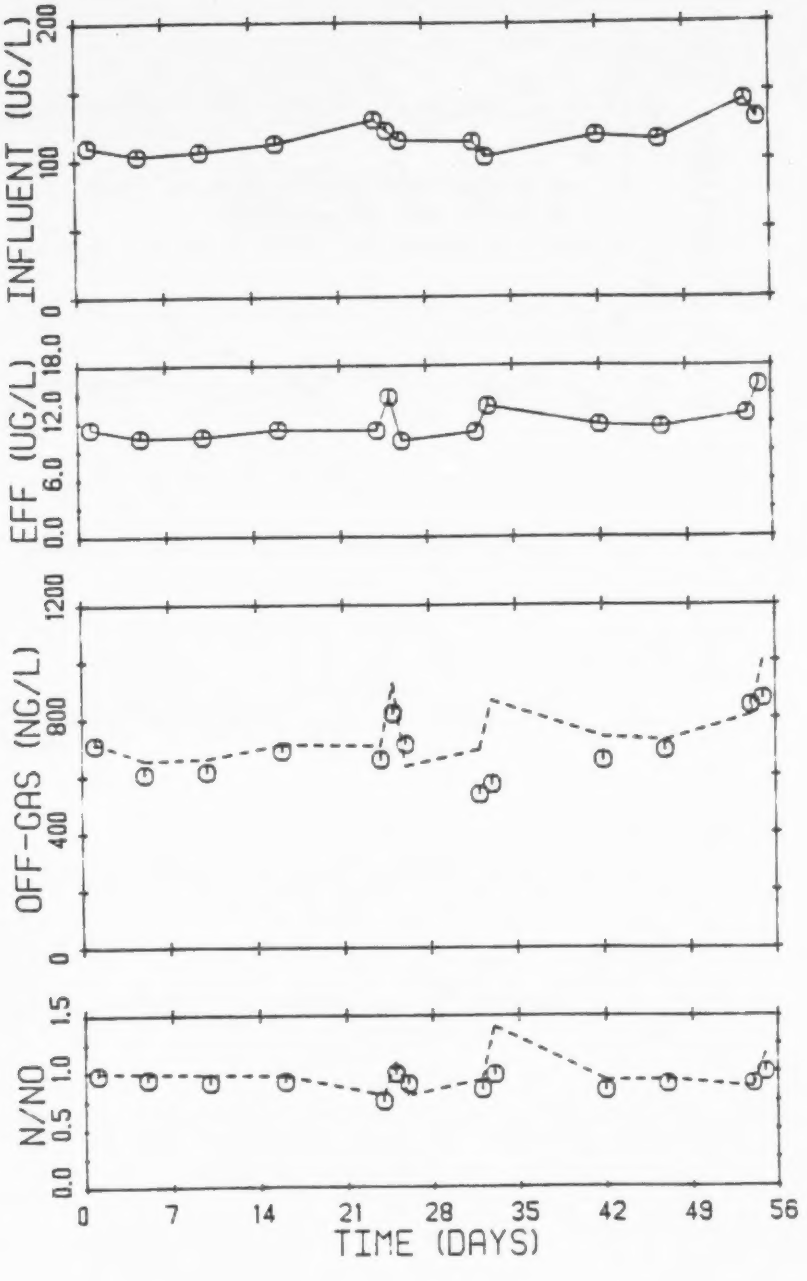


FIGURE 10-14. 1,2,4-Trichlorobenzene off-gas concentrations and N/N_o values predicted from effluent concentrations measured during the 6-day SRT activated sludge study. (Dashed lines give predicted values.)

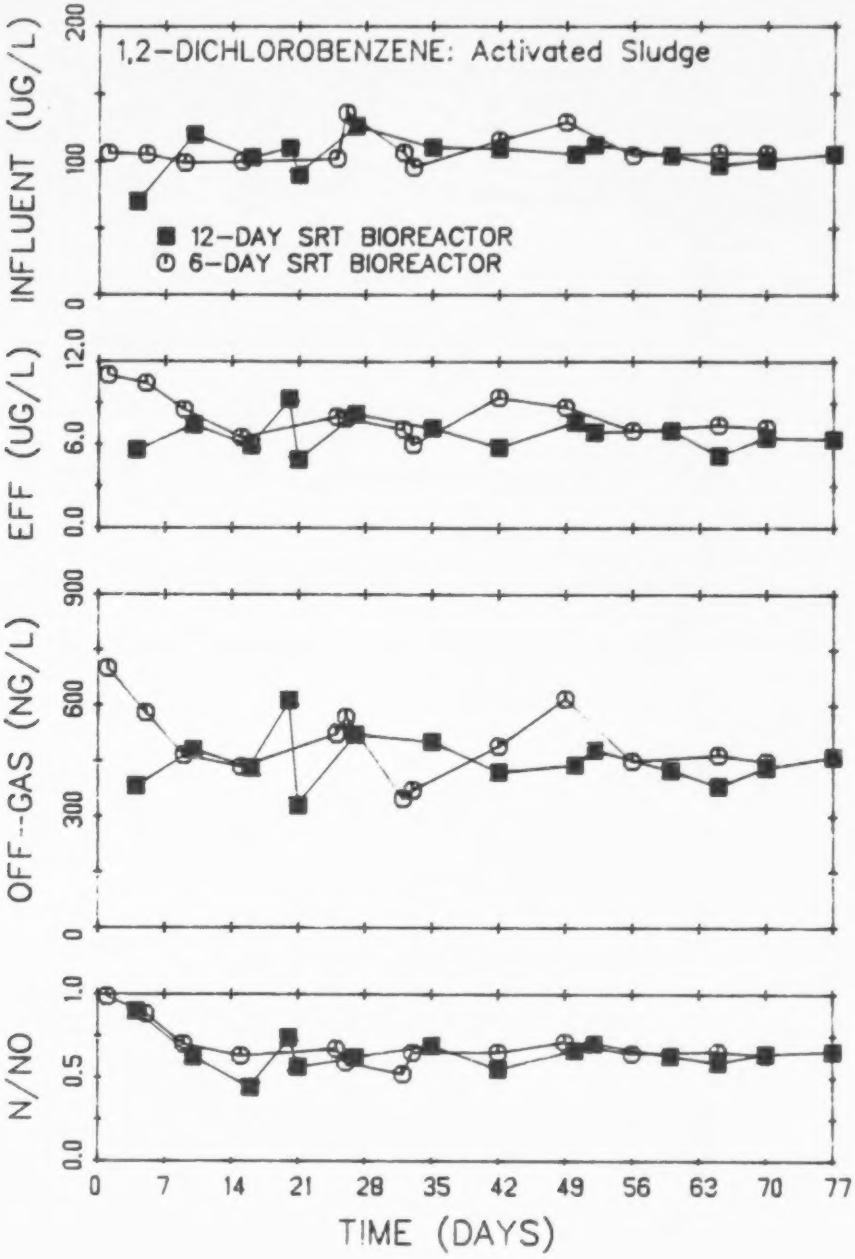


FIGURE 10-15. 1,2-Dichlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries (N/N_o) from 6 and 12-day SRT activated sludge studies.

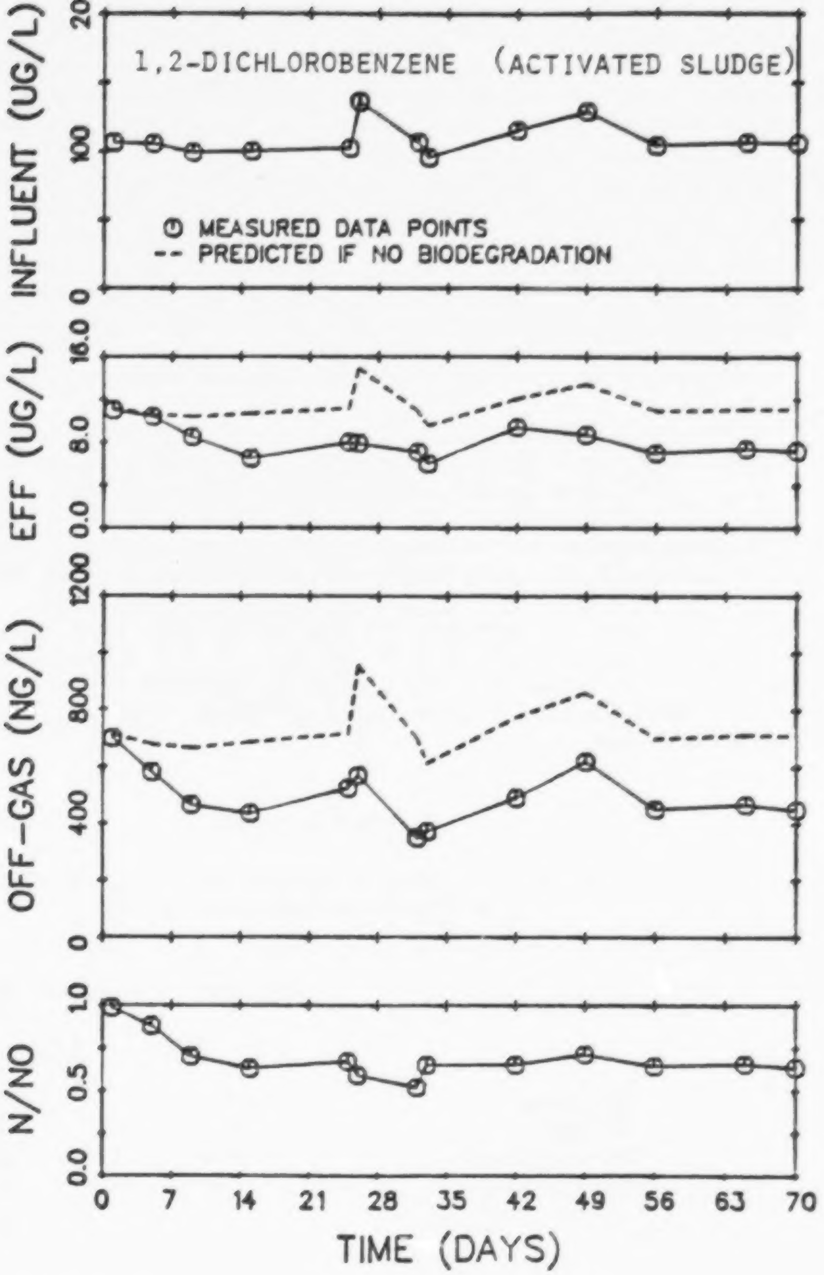


FIGURE 10-16. Influent, effluent, and off-gas concentrations and N/N_o values from a 6-day SRT activated sludge study conducted in a 10-liter bioreactor.

a disappearance of 1,2-dichlorobenzene from the experimental system. Baseline studies conducted without activated sludge under similar conditions demonstrated average recoveries in excess of 90%. The disappearance of 1,2-dichlorobenzene was attributed to biodegradation by activated sludge microorganisms. As shown by the results in Figure 10-15, fractional recoveries of 1,2-dichlorobenzene began at approximately 0.90 on Day 1 indicating a near complete recovery and no biodegradation. During the first 14 days of the studies the fractional recovery steadily decreased to a steady-state value of 0.62. Both effluent and off-gas concentrations decreased during acclimation periods by approximately 38%. The effect of biodegradation on the fate of 1,2-dichlorobenzene is shown in Figure 10-17 which compares the effluent and off-gas fluxes to the amount removed by biodegradation during the 6-day SRT study. Effluent and off-gas fluxes averaged 6.8% and 56.2% respectively, in the 6 and 12-day SRT studies combined compared with a 37.0% removal of 1,2-dichlorobenzene due to biodegradation.

Results observed in the 6 and 12-day SRT units were not significantly different as shown by the comparison presented in Figure 10-15. Table 10-9 summarizes influent, effluent, and off-gas values averaged from periods of steady-state 1,2-dichlorobenzene biodegradation following acclimation of the microorganisms. Influent concentrations averaged nearly 110 μg/ℓ while effluent concentrations averaged 7.8 and 6.8 μg/ℓ, respectively, in the 6 and 12-day SRT studies. Off-gas concentrations were between 470 and 480 ng/ℓ in both studies. Table 10-10 provides a comparison of the fate of 1,2-dichlorobenzene in the two bioreactor studies. The amount biodegraded was calculated from a reactor mass balance from measured influent, effluent, and off-gas concentrations.

TABLE 10-10

FATE OF 1,2,-DICHLOROBENZENE IN 6 AND 12-DAY SRT ACTIVATED SLUDGE BIOREACTORS

	PERCENT OF INFLUENT FLUX	
	6-Day SRT	12-Day SRT
Effluent	7.1	6.4
Off-Gas	56.3	56.1
Biodegraded	36.6	37.5
Biosorbed	0	0

In an effort to demonstrate that the disappearance of 1,2-dichlorobenzene was not due to an experimental anomaly, 1,2,4-trichlorobenzene was added to the influent of the 12-day SRT activated sludge unit. Recovery of 1,2,4-trichlorobenzene averaged greater than 90% during the two-week period it was added to the influent.

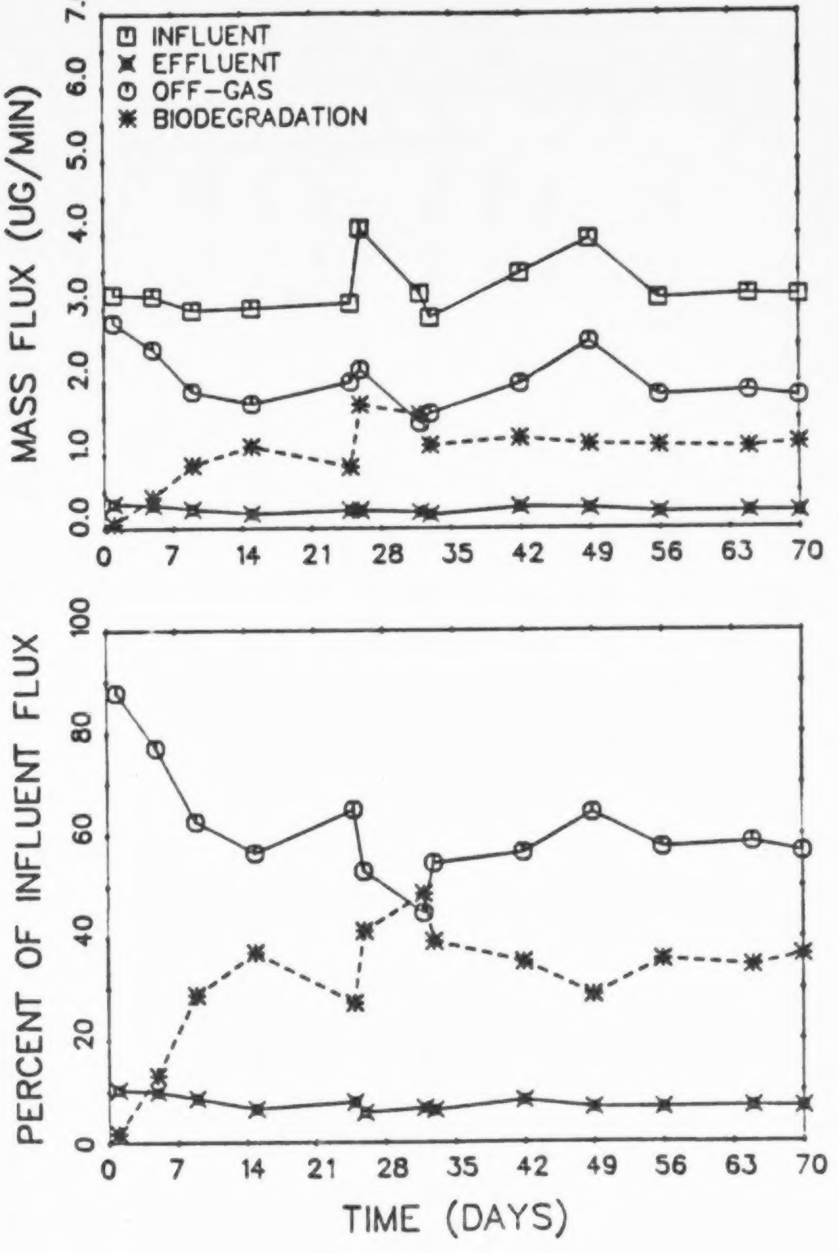


FIGURE 10-17. Influent, effluent, and off-gas fluxes and amounts of 1,2-dichlorobenzene removed by biodegradation during the 6-day SRT activated sludge study.

TABLE 10-9

COMPARISON OF MEASURED AND PREDICTED STEADY-STATE EFFLUENT AND OFF-GAS 1,2-DICHLOROBENZENE CONCENTRATIONS FROM ACTIVATED SLUDGE BIOREACTORS

	Influent (μg/ℓ)	Effluent (μg/ℓ)	Off-Gas (ng/ℓ)	N/N_o
	6-DAY SRT BIOREACTOR			
Measured	+109.7 (13.3)	7.8 (1.5)	477 (93)	0.63 (0.06)
Predicted if no biodegradation	--	11.7 (1.7)	736 (101)	1.00 (0.00)
Predicted from effluent	--	--	483 (90)	0.65 (0.08)
	12-DAY SRT BIOREACTOR			
Measured	107.1 (9.4)	6.8 (1.2)	471 (61)	0.62 (0.08)
Predicted if no biodegradation	--	10.9 (1.0)	699 (64)	1.00 (0.00)
Predicted from effluent	--	--	435 (78)	0.61 (0.08)

+ Mean

( ) Standard Deviation

The air-stripping model was used to predict off-gas concentrations and N/N_0 values from measured effluent concentrations for the 1,2-dichlorobenzene activated sludge studies. As shown by the comparison in Figure 10-18, there was excellent agreement between predicted and measured values during the 6-day SRT study. Measured off-gas concentrations and N/N_0 values averaged 477 μg/ℓ and 0.63, respectively, compared with predicted values of 483 ng/ℓ and 0.65. A summary of off-gas concentrations and N/N_0 values predicted from effluent measurements has been included in Table 10-9. These results demonstrate the ability of the air-stripping model to predict the disappearance of a volatile, poorly-degradable compound. This finding suggests that the fate of 1,2-dichlorobenzene could have been well-characterized without the continual monitoring of the amounts stripped to the atmosphere. The accuracy with which off-gas concentrations could be predicted was dependent upon two important factors: 1) well characterized volatilization rate parameters, and 2) analytical techniques which enabled accurate determinations of low part-per-billion concentrations of 1,2-dichlorobenzene in the effluent.

10.4 FATE OF BIODEGRADABLE COMPOUNDS DURING ACTIVATED SLUDGE TREATMENT

Significant biodegradation was found to occur for six compounds: benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, and nitrobenzene. Activated sludge bioreactor studies were conducted with each compound in the 10-liter bioreactors operated with 6-day solids retention times. Additional studies were run at solids retention times of 3 and 12-days with selected toxics. Initial activated sludge studies were conducted with only a single toxic organic in the influents while later multi-solute studies involved the addition of two or more compounds to the influents.

10.4.1 Non-volatile Compound: Nitrobenzene

Results from baseline volatilization studies in 10-liter bioreactors without activated sludge showed only a small amount of nitrobenzene was stripped to the atmosphere. Reductions in the aqueous concentrations averaged approximately 20% at operating conditions of 4 ℓ/min aeration, 5.5 hour hydraulic retention time, and a 100 μg/ℓ influent nitrobenzene concentration. Initial activated sludge studies with nitrobenzene included off-gas analyses but since steady-state nitrobenzene off-gas fluxes represented only a very small fraction of the influent loadings, later studies did not include off-gas sampling.

Nitrobenzene activated sludge studies were conducted in bioreactors operated at 6-day solids retention times. Results from an activated sludge study presented in Figure 10-19 include influent and effluent concentrations and C_e/C_i values, the ratio of effluent to influent concentrations. There was no significant difference between steady-state C_e/C_i and N/N_0 values because the off-gas contribution to the flux out of the reactor was small. Effluent concentrations averaged less than 3 μg/ℓ in activated sludge studies with influent nitrobenzene

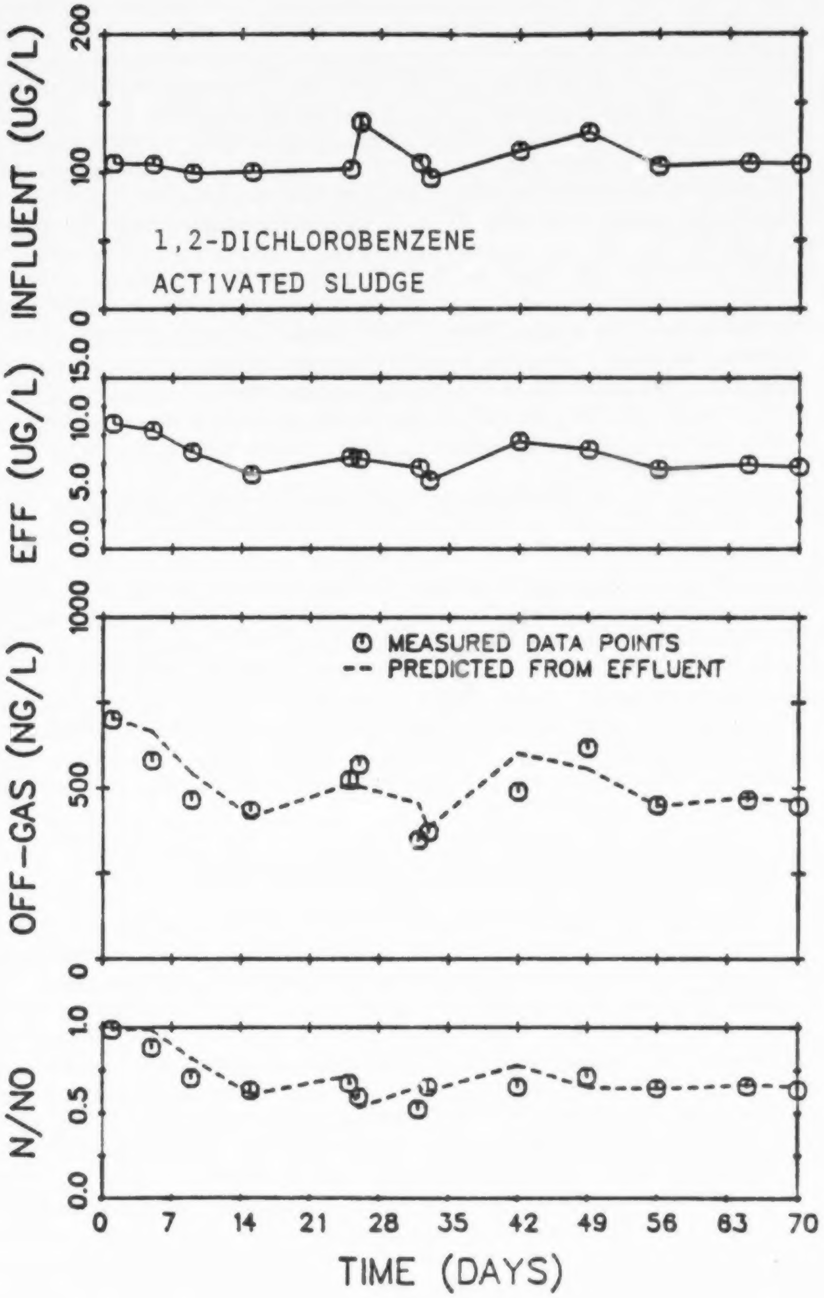


FIGURE 10-18. Experimental data and off-gas concentrations and N/N_o values predicted from measured effluent concentrations for the 6-day SRT activated sludge study with 1,2-dichlorobenzene.

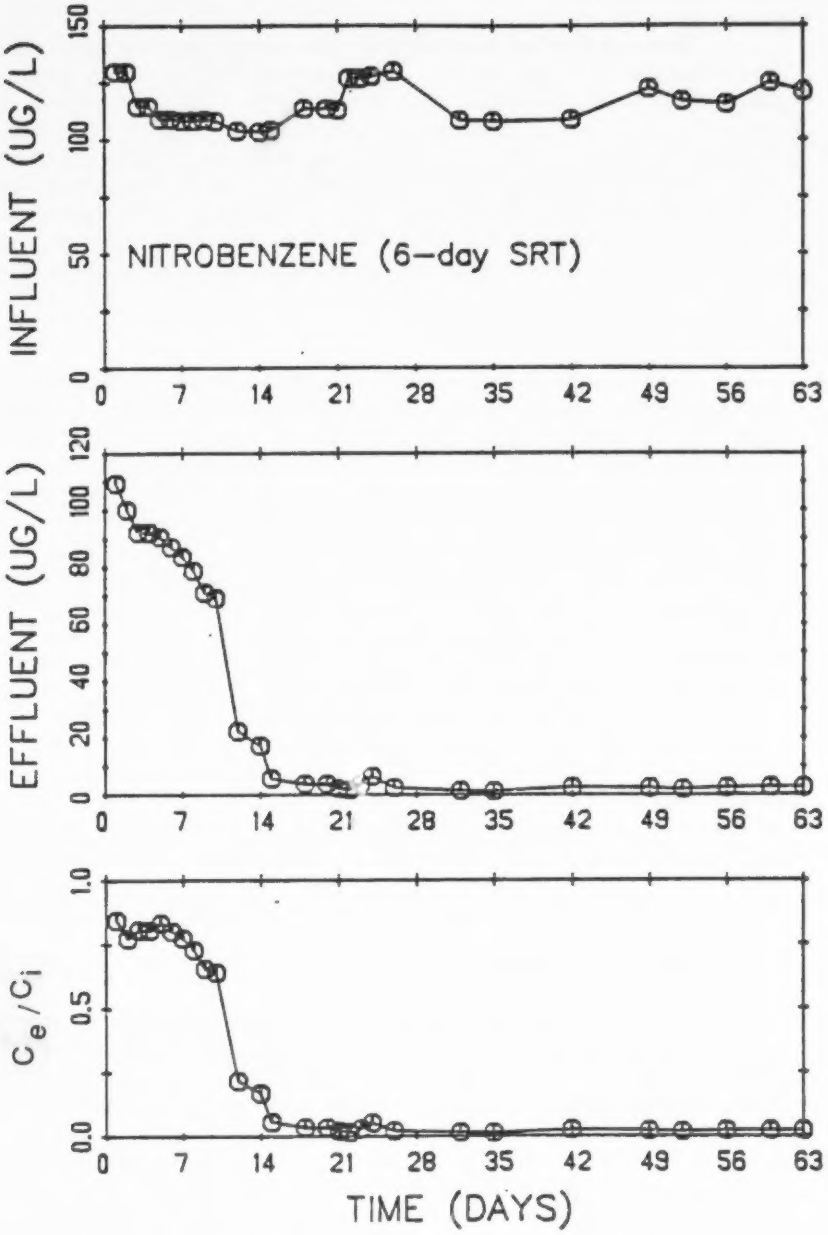


FIGURE 10-19. Nitrobenzene influent and effluent concentrations and ratio of effluent to influent concentrations, C_e/C_i, during a 6-day SRT activated sludge study.

levels between 100 and 120 μg/ℓ; off-gas concentrations typically were less than 10 ng/ℓ. Biodegradation effected overall nitrobenzene removals of 95 to 97%. A summary of steady-state results for the 63-day activated sludge study is given in Table 10-11

The activated sludge studies exhibited an approximate two week acclimation period prior to steady-state nitrobenzene removal by microbial degradation. Day 1 analyses resulted in near complete recoveries (effluent and off-gas fluxes combined) indicating no biodegradation. Nitrobenzene recovery decreased dramatically between Day 7 and 14 from greater than 80% to less than 5% as the activated sludge developed the capability to degrade nitrobenzene. Once a steady-state biodegradation rate was established, the bioreactor performance with respect to nitrobenzene removal was consistently good.

10.4.2. Volatile Compounds

Results from activated sludge studies conducted with the volatile compounds benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene have been presented in figures which include influent, effluent, and off-gas concentrations, and N/N_0 values representing the fraction of the influent mass fluxes measured leaving the bioreactors in the effluents and off-gases combined. The addition of the toxic organic compound to the influent was begun on Day 0 in each case. Plotted as dashed lines in various figures are effluent and off-gas concentrations predicted by the air-stripping model to occur if only volatilization effected a reduction in the aqueous concentration in which case $N/N_0 = 1.0$ and a complete recovery would occur. Background studies conducted in the experimental bioreactors without activated sludges indicated that average recoveries of each compound were approximately 95%. Recoveries less than 90%, or N/N_0 values less than .90, were considered evidence of biological degradation. The overall removal or disappearance of a compound, defined as the fraction of the influent flux not found in effluents, off-gases, and waste sludges combined, was used as a measure of the amount of the compound biodegraded. Batch biodegradation studies with acclimated sludges were conducted to confirm that biological degradation of the compounds was occurring in the CMF bioreactors.

10.4.2.1. Benzene

Activated sludge studies with benzene were conducted in 10-liter bioreactors maintained at three solids retention times: 3, 6, and 12-days. Each study was conducted for at least seven weeks after benzene was added to the influent wastewater. The three activated sludge bioreactors were not run concurrently but rather they spanned a period of approximately 18 months. Results from the 3,6 and 12-day SRT studies are presented in Figures 10-20, 10-21, and 10-22, respectively. Each figure includes: 1) measured influent, effluent, and off-gas concentrations connected by solid lines; 2) dashed lines representing effluent and off-gas concentrations predicted assuming no biodegradation occurred and only volatilization effected a reduction in the aqueous concentration of benzene; and, 3) N/N_0 values representing the fraction of the influent benzene measured leaving the bioreactors in effluents and off-gases combined.

TABLE 10-11

SUMMARY OF INFLUENT, EFFLUENT AND OFF-GAS CONCENTRATIONS OF NITROBENZENE FROM AN ACTIVATED SLUDGE REACTOR OPERATED WITH A 6-DAY SRT

Parameter	Mean +	Standard Deviation
Influent (μg/ℓ)	117.8	8.0
Effluent (μg/ℓ)	2.6	1.4
Off-Gas (ng/ℓ)	9.0	4.1
C_e/C_i	0.024	0.013
N/N_o	0.026	0.015
Reduction in Aqueous Conc. (%)	97.6	1.3
Overall Removal (%)	97.4	1.5
Hydraulic Retention Time (hours)	5.6	--
Aeration Rate (ℓ/min)	4.0	--
MLSS (mg/l)	3360	

+ Data summarized from Days 14 to 63

While baseline studies without activated sludge demonstrated that the average recovery of benzene was greater than 90% ($N/N_0>0.90$), maximum recoveries of benzene in the 3,6, and 12-day SRT activated sludge studies ranged from only 50 to 60% ($N/N_0 \approx 0.50$ to 0.60). The disappearance of benzene resulted in measured effluent and off-gas concentrations that were considerably less than the predicted values as illustrated by the differences between the dashed lines and the data points in Figures 10-20 through 10-22. Batch equilibrium sorption studies showed no significant sorption of benzene by the activated sludge biomass. The disappearance of benzene was attributed to biodegradation by activated sludge microorganisms. Biodegradation was confirmed in batch biodegradation rate studies.

Effluent and off-gas concentrations to some degree reflected variations in influent concentrations; therefore N/N_0 values were used to assess overall activated sludge performance with respect to benzene removal. The N/N_0 plots in Figures 10-20 through 10-22 showed two distinct phases. During the first 14 to 21 days, Phase I, the N/N_0 values decreased from approximately 0.50 to less than 0.20 indicating that the overall amount of benzene removed from the bioreactors increased from 50% to greater than 80%. This two to three week period was indicative of an acclimation phase when microorganisms in the activated sludge were becoming more effective at removing benzene. Phase II was characterized by relatively constant N/N_0 values indicating a period of steady-state benzene removal. Steady-state toxics removal was defined as no significant change in N/N_0 values during a period of time equal to three times the solids retention time. There was no difference in steady-state bioreactor performance with respect to benzene removal at the three SRT values evaluated as shown by the comparisons in Figures 10-23 and 10-24. Overall steady-state benzene removal, defined as $100x[1-(N/N_0)]$, averaged 83.6, 83.1, and 83.6% in the 3, 6, and 12-dav SRT units, respectively, during approximately five weeks of steady-state operation. Overall removals measured in the three activated sludge studies have been compared in Figure 10-25.

A summary of steady-state results from each activated sludge study is given in Table 10-12. Average influent concentrations ranged from 112 to 118 μg/ℓ while effluent and off-gas concentrations averaged less than 1.0 μg/ℓ and 150 ng/ℓ, respectively, in each study.

Benzene removal during the acclimation periods was found to be more variable than during steady-state operating periods. The N/N_0 values measured during the acclimation periods of the 6 and 12-day SRT studies were similar to each other but different from the values recorded in the 3-day SRT study. From initial values of approximately 0.50 on Day 1 the N/N_0 values constantly decreased to less than 0.20 in the 6 and 12-day SRT bioreactors. The N/N_0 values in the 3-day SRT unit fluctuated between 0.53 and 0.59 for the first ten days before decreasing to their steady-state levels.

The effect of biodegradation on the fate of benzene is readily apparent by comparing the measured effluent and off-gas concentrations

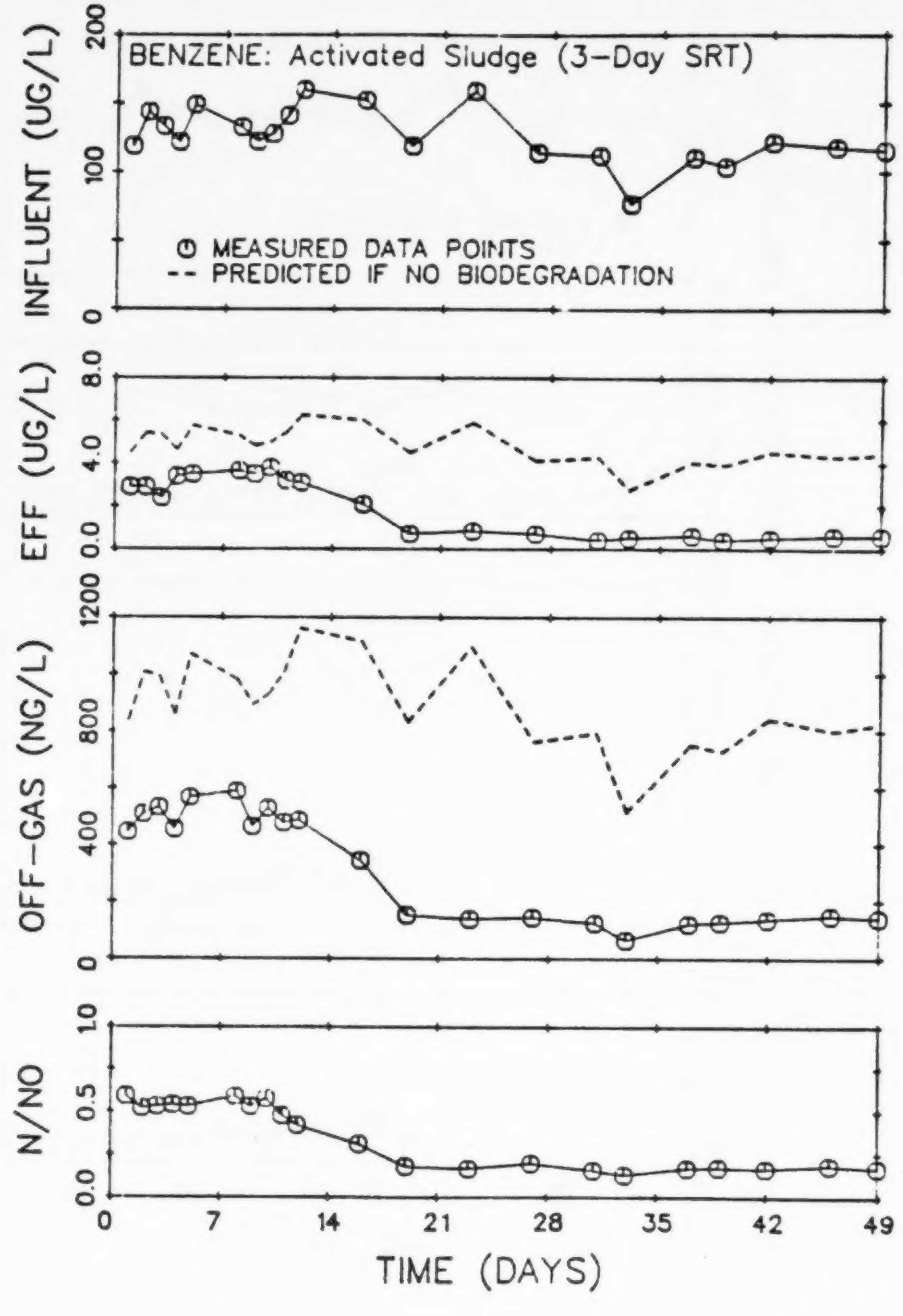


FIGURE 10-20. Benzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the 3-day SRT activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

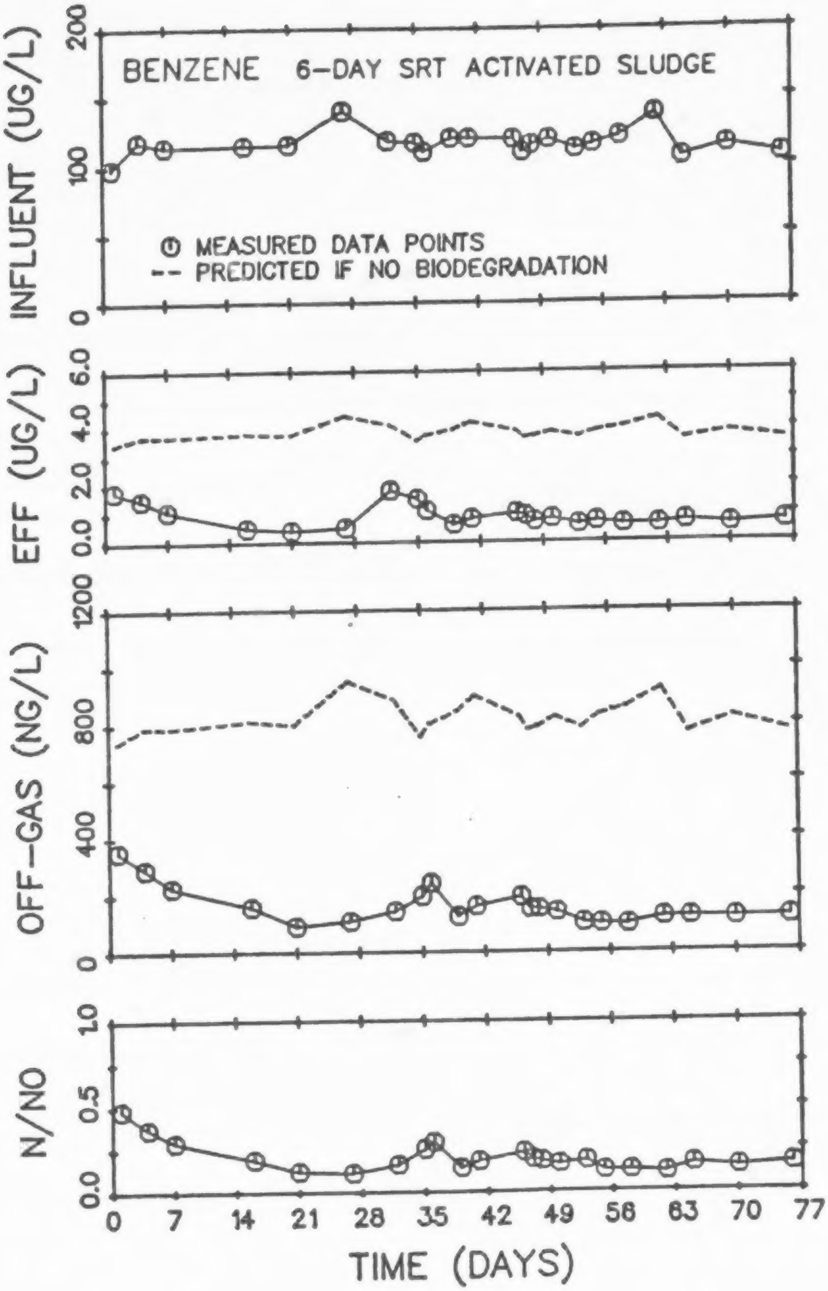


FIGURE 10-21. Benzene influent, effluent, and off-gas concentrations and fractional recoveries, N/N_0, measured during a 6-day SRT activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

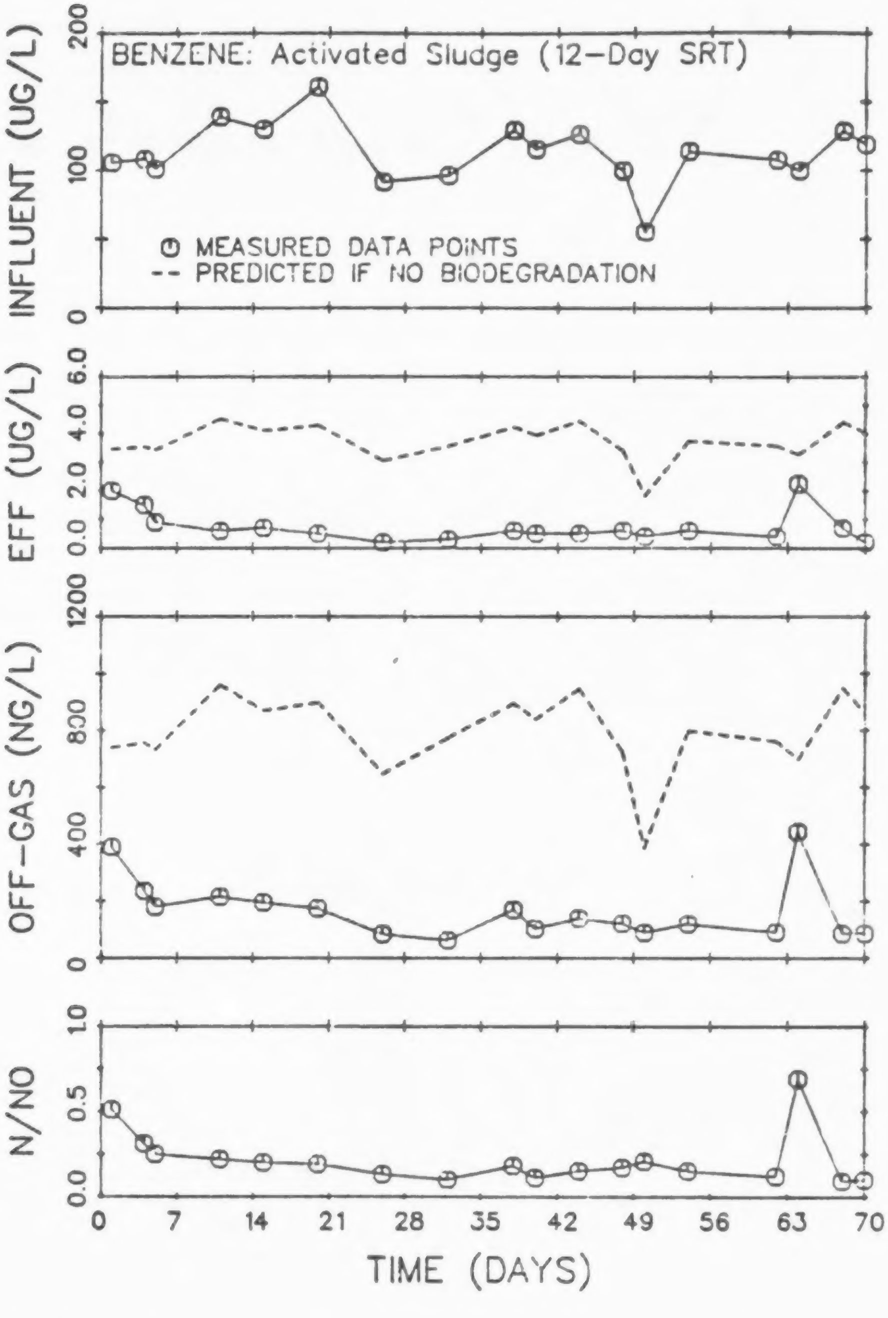


FIGURE 10-22. Benzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the 12-day SRT activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

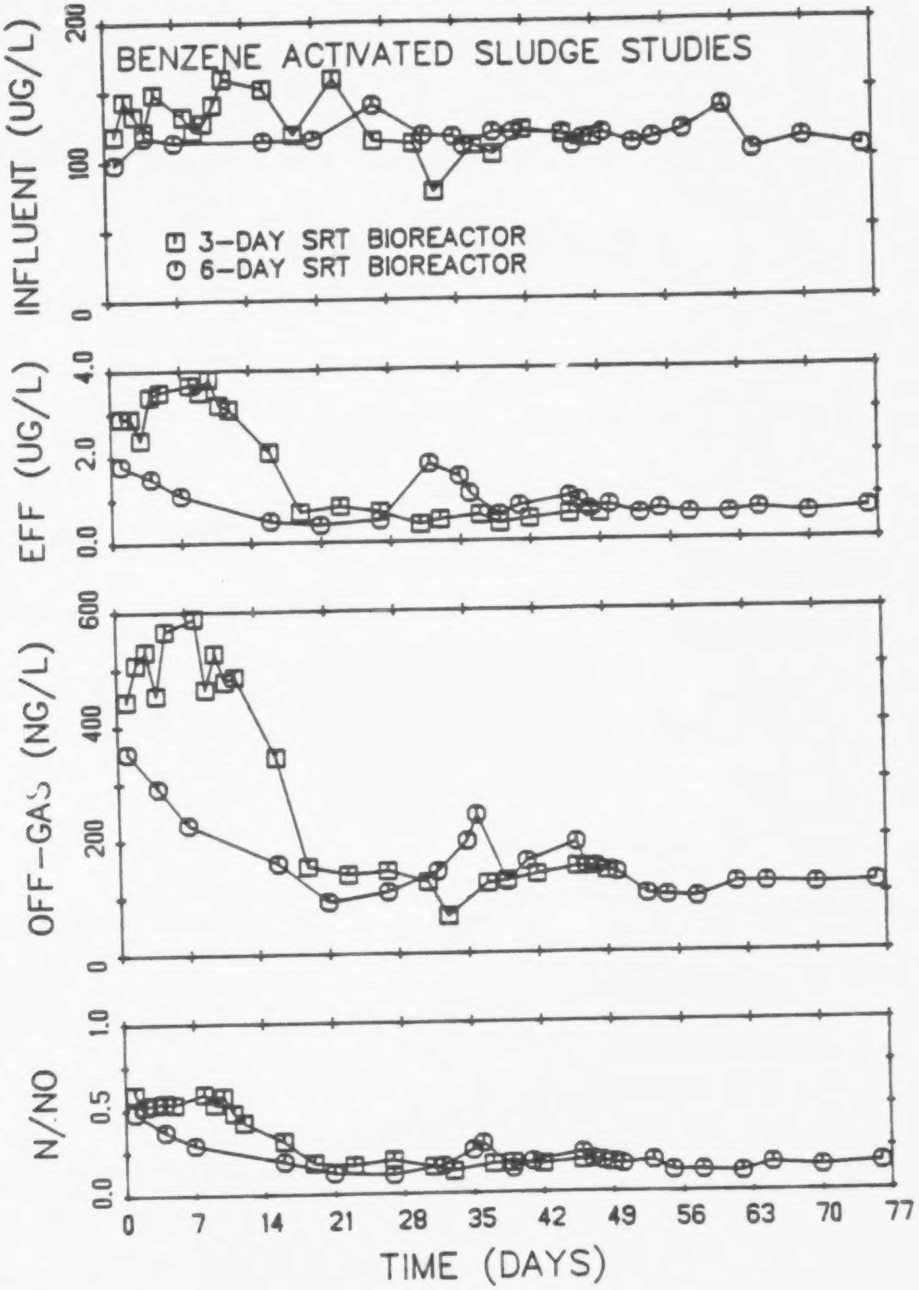


FIGURE 10-23. Comparison of influent, effluent, and off-gas concentrations and fractional recoveries, N/No, from benzene activated sludge studies conducted in 10-liter bioreactors operated with 3 and 6-day SRT's.

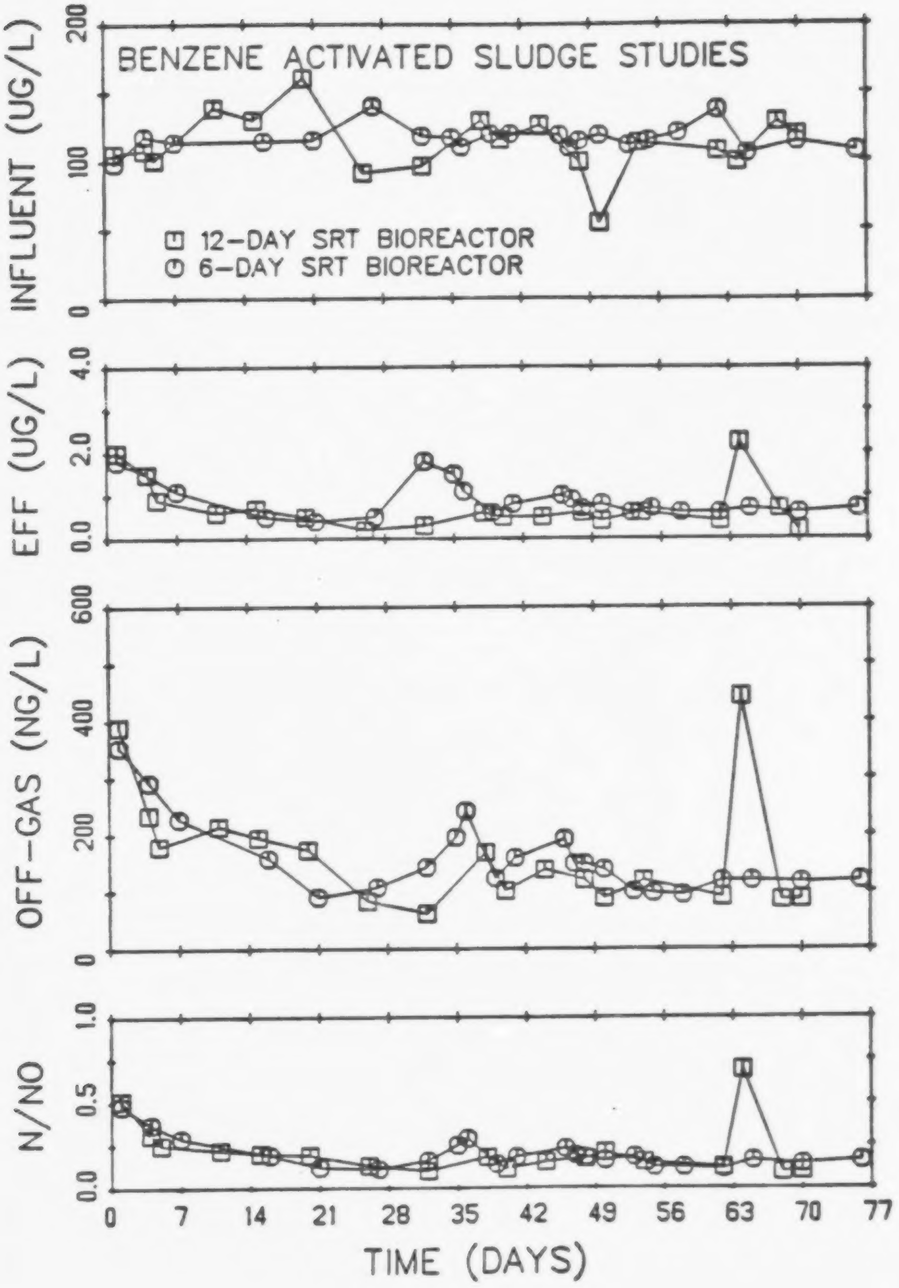


FIGURE 10-24. Comparison of influent, effluent, and off-gas concentrations and fractional recoveries, N/No, from benzene activated sludge studies conducted in 10-liter bioreactors operated with 6 and 12-day SRT's.

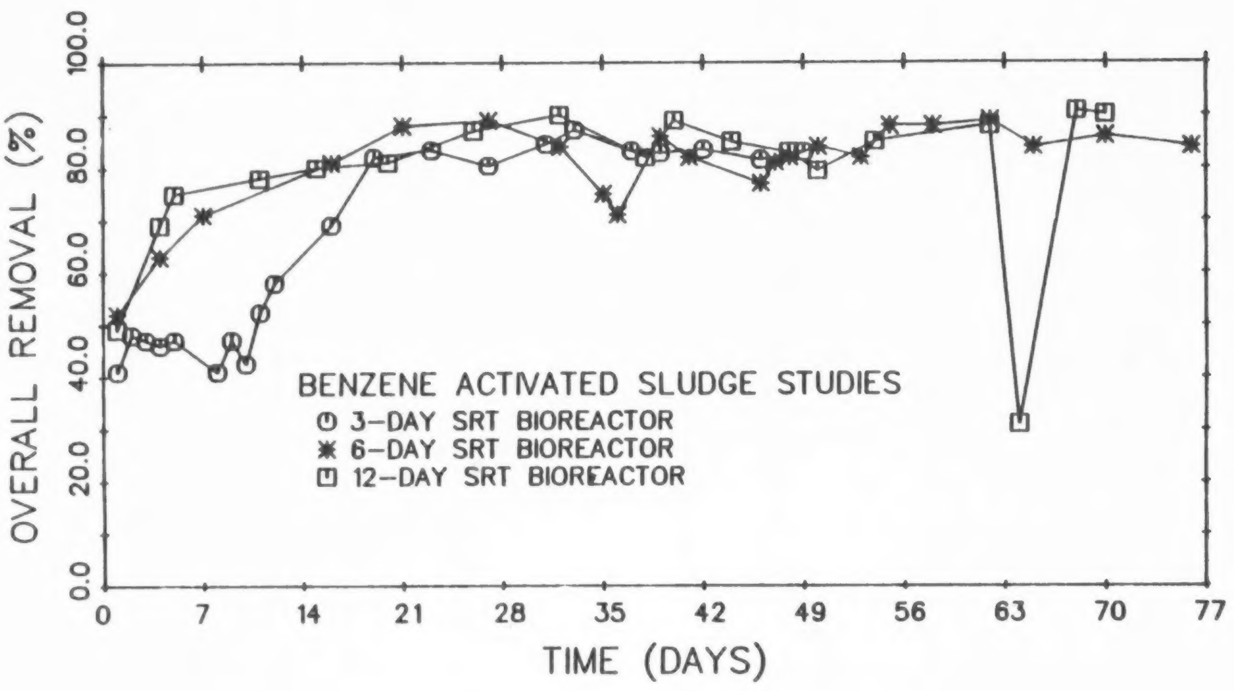


FIGURE 10-25. Overall benzene removals due to biodegradation measured during activated sludge studies conducted in 10-liter bioreactors operated with 3, 6, and 12-day SRT's.

TABLE 10-12

COMPARISON OF MEASURED AND PREDICTED STEADY-STATE EFFLUENT AND OFF-GAS BENZENE CONCENTRATIONS FROM ACTIVATED SLUDGE BIOREACTORS

	Influent (μg/ℓ)	Effluent (μg/ℓ)	Off-Gas (ng/ℓ)	N/N_o (-)	Removal (%)
		3-DAY SRT BIOREACTOR			
Measured	115.3(19.9)	0.6(0.1)	128(25)	0.164(0.021)	83.6(2.1)
Predicted if no biodegradation	--	4.3(0.8)	794(143)	1.00(0.0)	0.0(0)
Predicted from effluent	--	--	110(23)	0.140(0.026)	86.0(2.6)
		6-DAY SRT BIOREACTOR			
Measured	117.8(8.4)	0.8(0.4)	141(40)	0.169(0.052)	83.1(5.2)
Predicted if no biodegradation	--	4.4(0.3)	814(56)	1.00(0.0)	0.0(0)
Predicted from effluent	--	--	139(49)	0.168(0.046)	83.2(4.6)
		12-DAY SRT BIOREACTOR			
Measured	112.5(24.4)	0.5(0.2)	116(41)	0.164(0.041)	83.6(4.1)
Predicted if no biodegradation	--	4.3(0.8)	806(150)	1.00(0.0)	0.0(0)
Predicted from effluent	--	--	91(31)	0.120(0.039)	88.0(3.9)

Data Summarized from Steady-State Operating Periods

3 day SRT Study -- Days 21 to 49
6 day SRT Study -- Days 21 to 77
12 day SRT Study -- Days 21 to 70

to the concentrations predicted if biodegradation had not occurred. Biodegradation caused reductions in effluent and off-gas concentrations of approximately 81 and 83%, respectively, during conditions of steady-state benzene removal. Measured on a mass flux basis, over 80% of the benzene that entered the bioreactors was biodegraded and less than 20% left the reactors in the off-gases. The effluent contribution to the mass fluxes out of the bioreactors was less than 1%. Figures 10-26, 10-27 and 10-28 compare the effluent and off-gas mass fluxes to the amount of benzene removed by biodegradation during the 3,6, and 12-day SRT activated sludge studies, respectively. The amount biodegraded was calculated by subtracting the effluent and off-gas fluxes from the influent fluxes. Table 10-13 summarizes the fate of benzene in each activated sludge study.

The importance of measuring off-gas fluxes to formulate a mass balance for each compound has been illustrated by the comparison of results for benzene and 1,2,4-trichlorobenzene with and without considering the amounts stripped to the atmosphere. Results for the two volatile compounds plotted by the more traditional method in Figure 10-29 of considering only influent and effluent concentrations and C_e/C_i values were quite similar and showed reductions in the aqueous concentration of 90% or greater for both compounds. This method does not facilitate interpretation of the specific removal mechanisms in the manner that the same data does in Figure 10-30 which includes off-gas concentrations. Readily apparent in Figure 10-30 is the effect of biodegradation on the fate of benzene which resulted in N/N_0 values less than 0.20, while N/N_0 values for the non-biodegradable 1,2,4-trichlorobenzene averaged greater than 0.90.

TABLE 10-13

FATE OF BENZENE IN 3,6-AND 12-DAY SRT
ACTIVATED SLUDGE STUDIES DURING STEADY-STATE
BIODEGRADATION

	Percent of Influent Flux		
	3-Day SRT	6-Day SRT	12-Day SRT
Effluent	0.5	0.7	0.4
Off-Gas	15.9	16.2	16.0
Biodegraded	83.6	83.1	83.6
Biosorbed	0	0	0

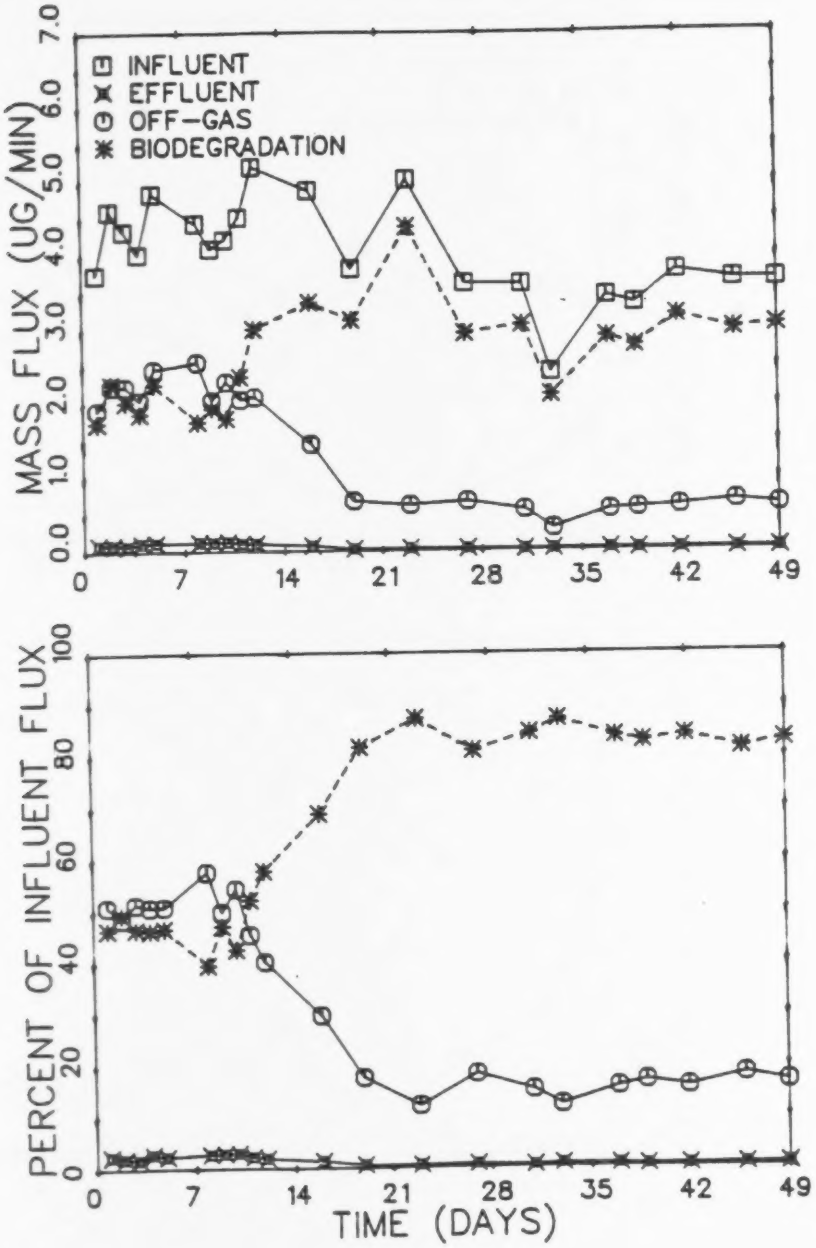


FIGURE 10-26. Benzene influent, effluent and off-gas fluxes and amounts removed by biodegradation during the 3-day SRT activated sludge study.

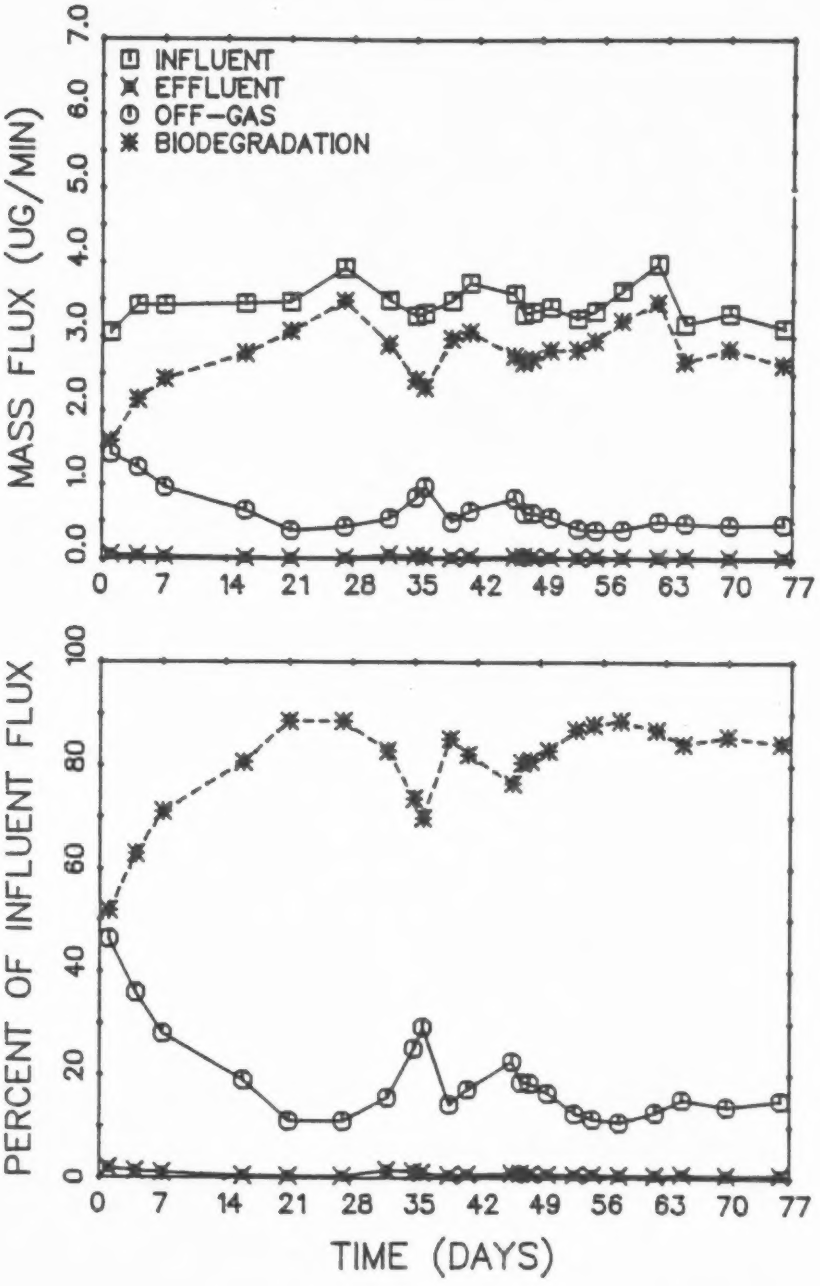


FIGURE 10-27. Benzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 6-day SRT activated sludge study.

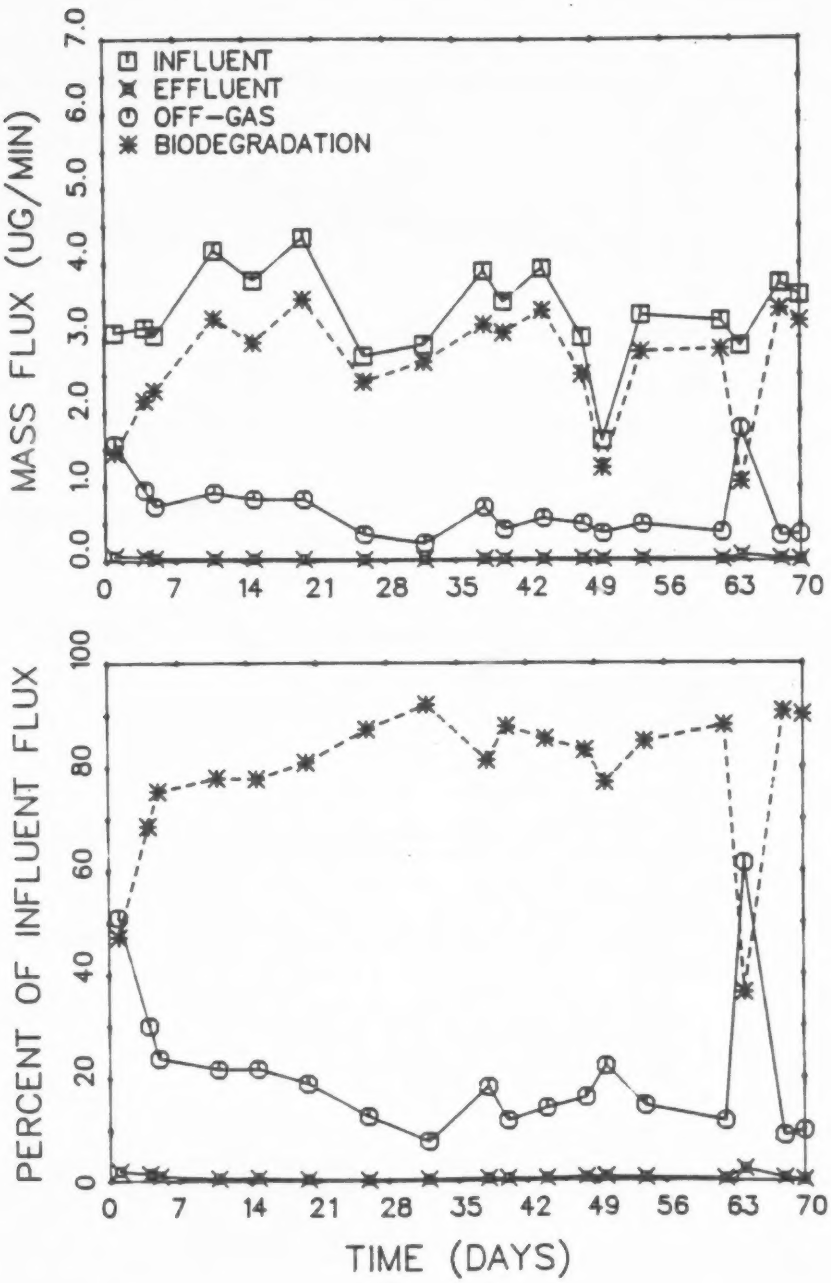


FIGURE 10-28. Benzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 12-day SRT activated sludge study.

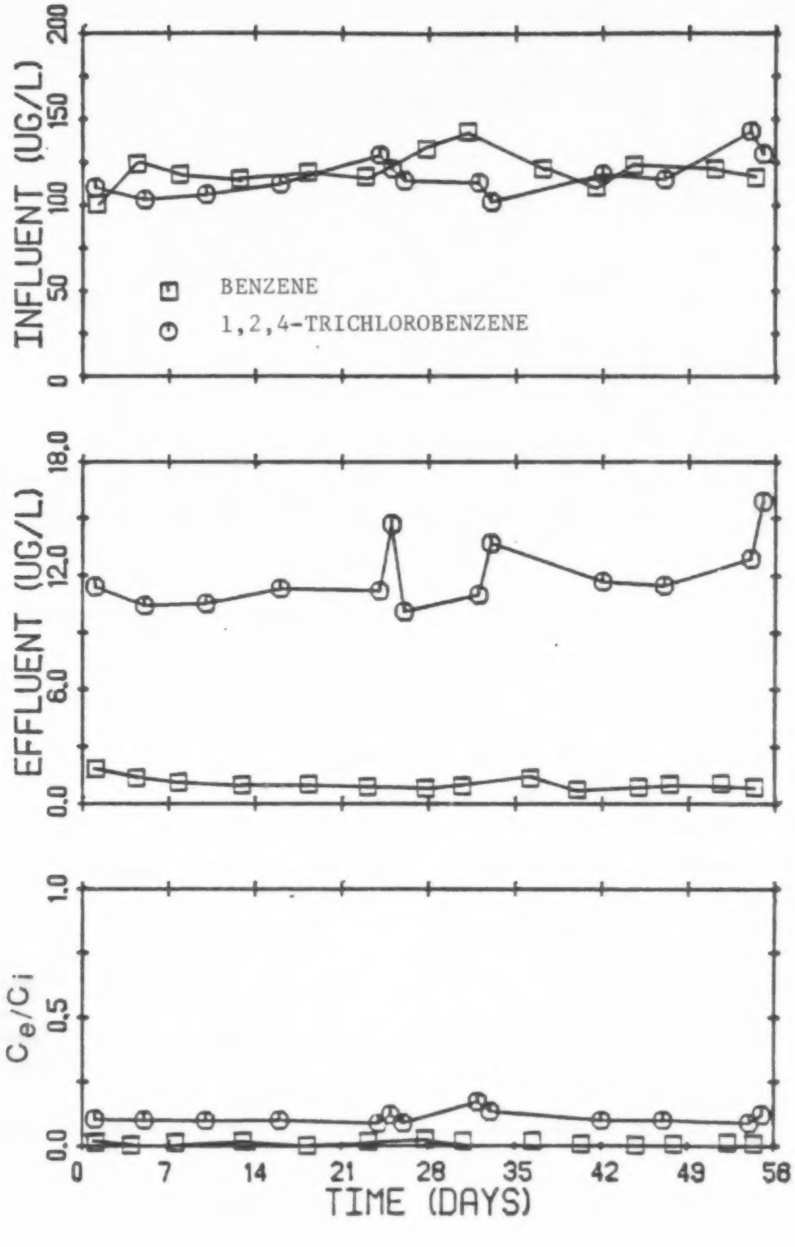


FIGURE 10-29. Comparison of benzene and 1,2,4-trichlorobenzene results from 10-liter bioreactor activated sludge studies without considering amounts of each compound stripped to the atmosphere in bioreactor off-gases (SRT=6 days)

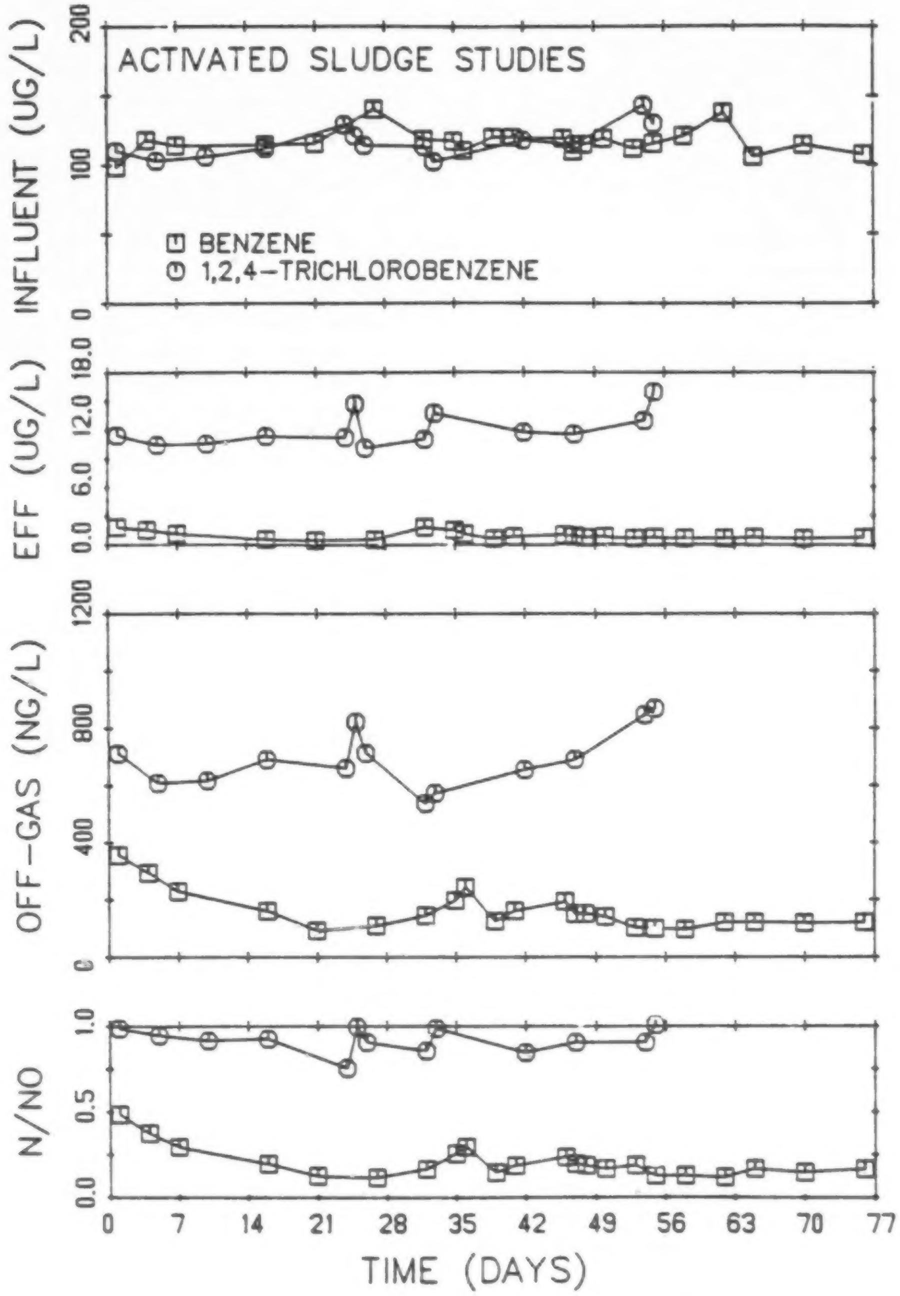


FIGURE 10-30. Benzene and 1,2,4-trichlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, from activated sludge studies conducted in 10-liter bioreactors operated with 6-day SRT's.

The fate of a trace, volatile biodegradable organic compound can be evaluated without measuring the off-gas concentrations if the air-stripping characteristics of the compound are known. Results for 1,2,4-trichlorobenzene showed that effluent concentrations could be used to accurately predict off-gas concentrations of a non-biodegradable compound. The results in Figures 10-31, 10-32 and 10-33 demonstrate that the same procedure can be applied to biodegradable compounds. Off-gas concentrations predicted from effluent values by the air stripping model were combined with measured effluent and influent concentrations to predict the N/N_0 values which were used to distinguish between air-stripping and biodegradation. The accuracy with which off-gas and N/N_0 values could be predicted was dependent upon the reliability of the effluent analyses. Table 10-12 includes a comparison of measured off-gas and N/N_0 values with the values predicted from the effluent analyses. The average off-gas concentration predicted from the effluent concentration averaged 139 ng/ℓ in the 6-day SRT study compared with a measured value of 141 ng/ℓ. Similar good agreement between predicted and measured values occurred for the other benzene activated sludge studies.

10.4.2.2. Toluene

The fate of toluene during activated sludge treatment was studied in activated sludge bioreactors operated with 6 and 12-day solids retention times. Influent, effluent, off-gas, and N/N_0 values for the 6-day SRT bioreactor study are presented in Figure 10-34 and summarized by Table 10-14. The results were nearly identical to those observed for benzene. There was an approximate two week acclimation period characterized by a gradual decrease in the N/N_0 values from 0.43 to approximately 0.16. The mean overall removal of toluene due to biodegradation during the steady-state operating period of the 6-day SRT study, Days 12 to 56, was 84%. Influent and effluent concentrations during that period averaged 120 and 0.8 µg/ℓ, respectively. The largest effluent concentration measured was 2.1 µg/ℓ on Day 1. Biodegradation was the dominant removal mechanism during the 12-day SRT activated sludge study, also. Effluent and off-gas concentrations, as shown in Figure 10-35, were significantly less than the values predicted to occur in the absence of biodegradation. As observed during the 6-day SRT study, the 12-day SRT unit experienced an initial acclimation phase following the addition of toluene to the influent on Day 0. Influent, effluent and off-gas concentrations averaged 101 µg/ℓ, 0.5 µg/ℓ and 127 ng/ℓ, respectively, during the period of steady-state toluene removal. Biodegradation effected an 83% removal of toluene during the 12-day SRT activated sludge study compared to 84% in the 6-day SRT bioreactor. As shown by the comparison of measured effluent and off-gas concentrations and N/N_0 values in Figure 10-36, there was no significant difference in the fate of toluene during the two studies. Influent, effluent, and off-gas concentrations averaged from data collected after the acclimation period are tabulated in Table 10-15. Table 10-16 summarizes the fate of toluene in this experimental activated sludge system.

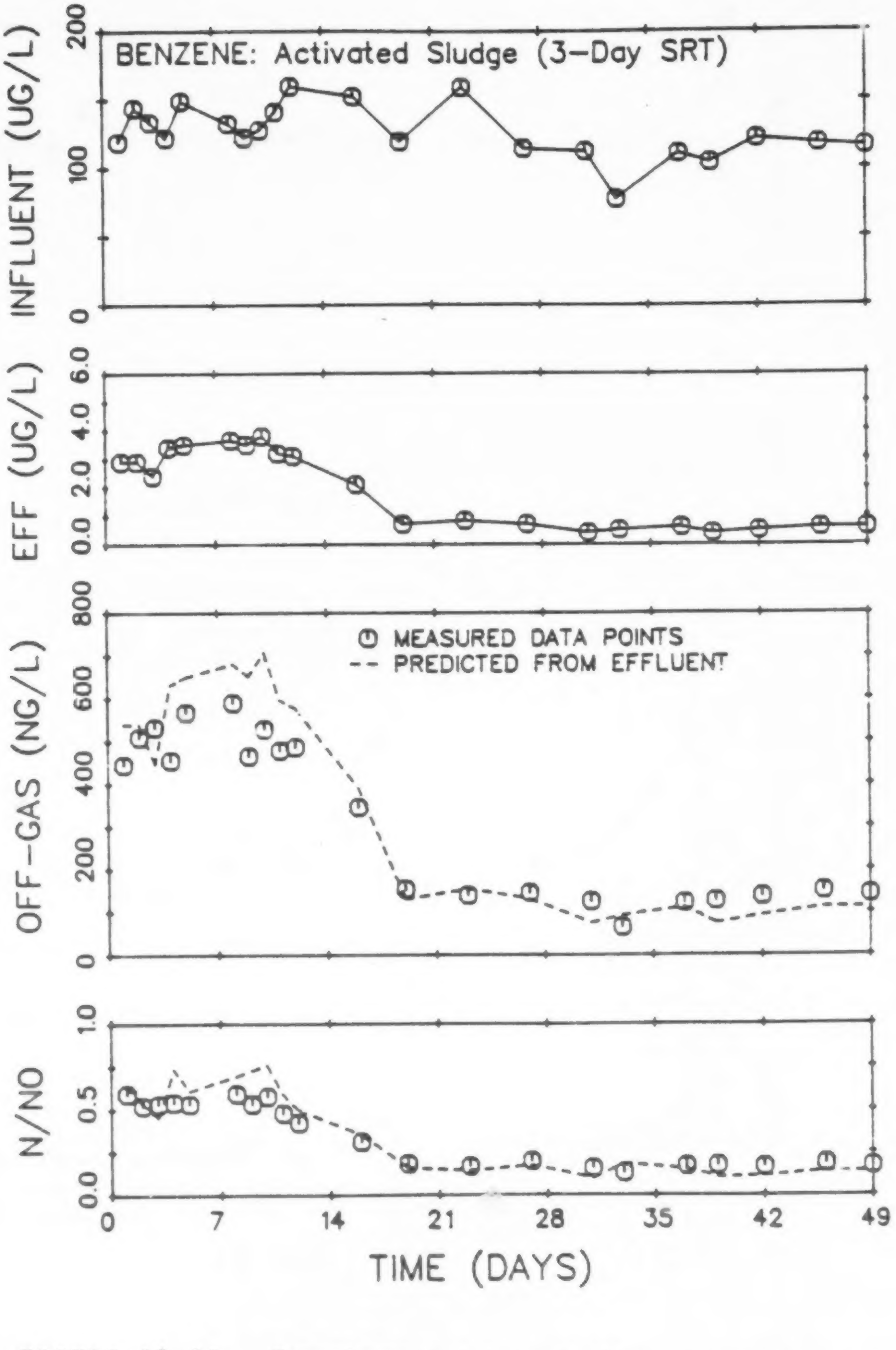


FIGURE 10-31. Experimental data and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 3-day SRT activated sludge study with benzene.

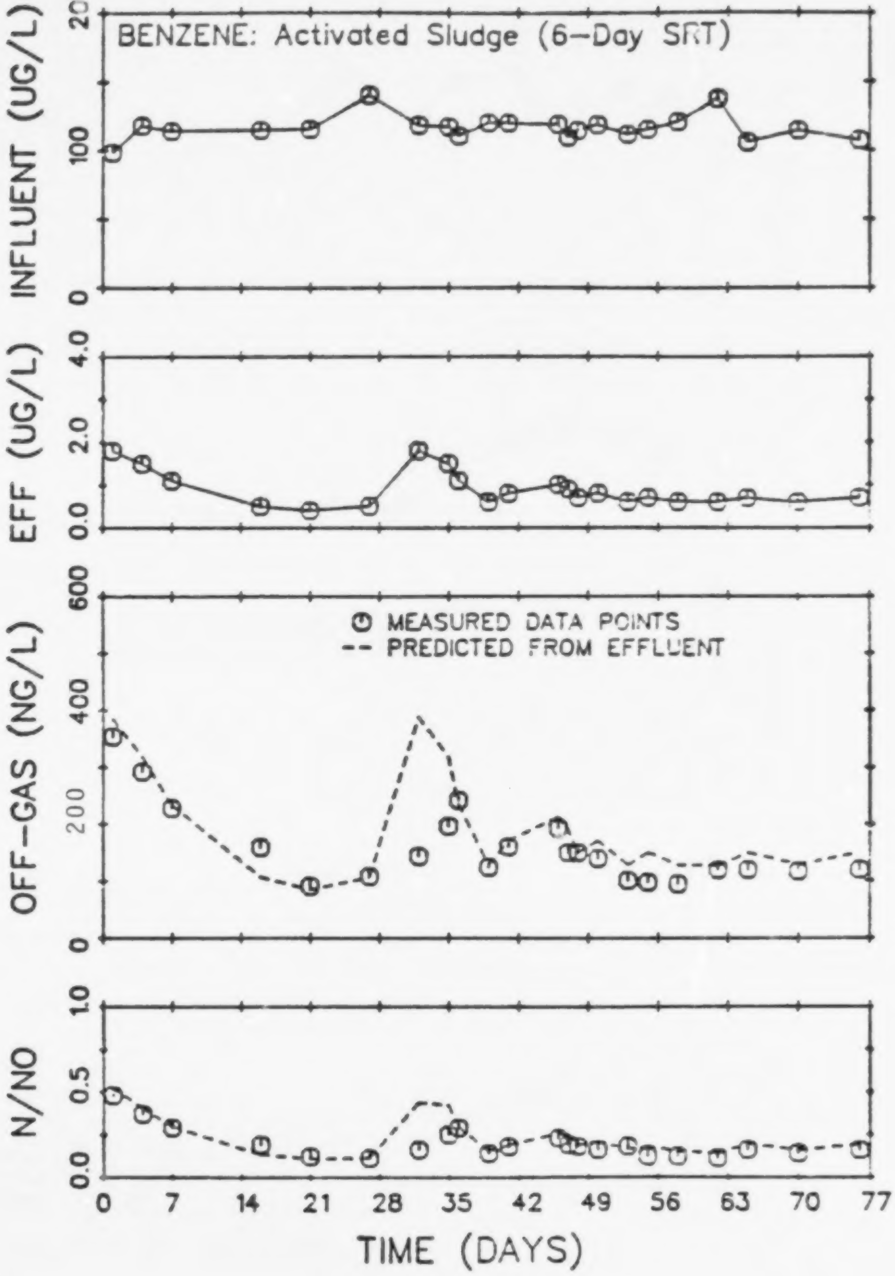


FIGURE 10-32. Experimental data and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 6-day SRT activated sludge study with benzene.

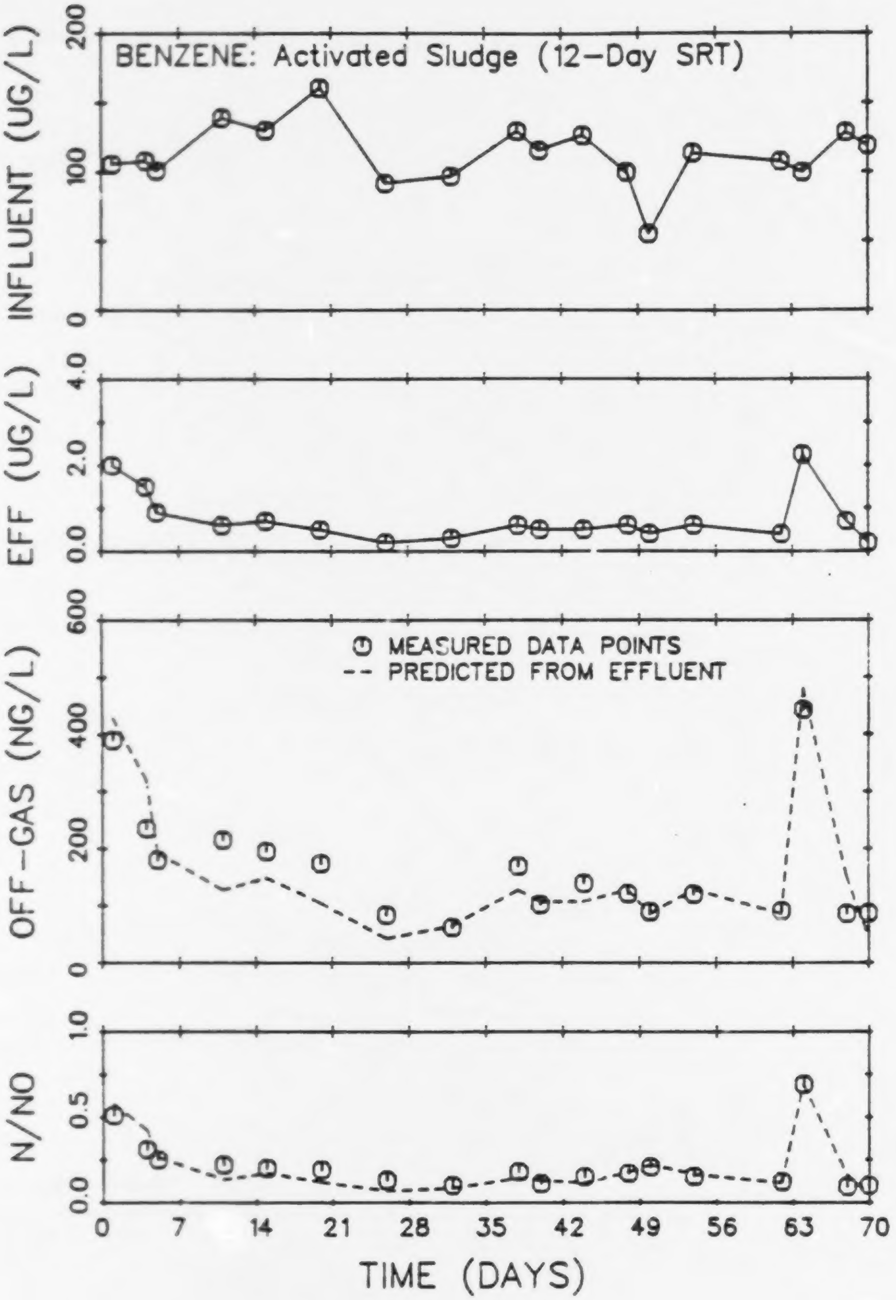


FIGURE 10-33. Experimental data and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 12-day SRT activated sludge study with benzene.

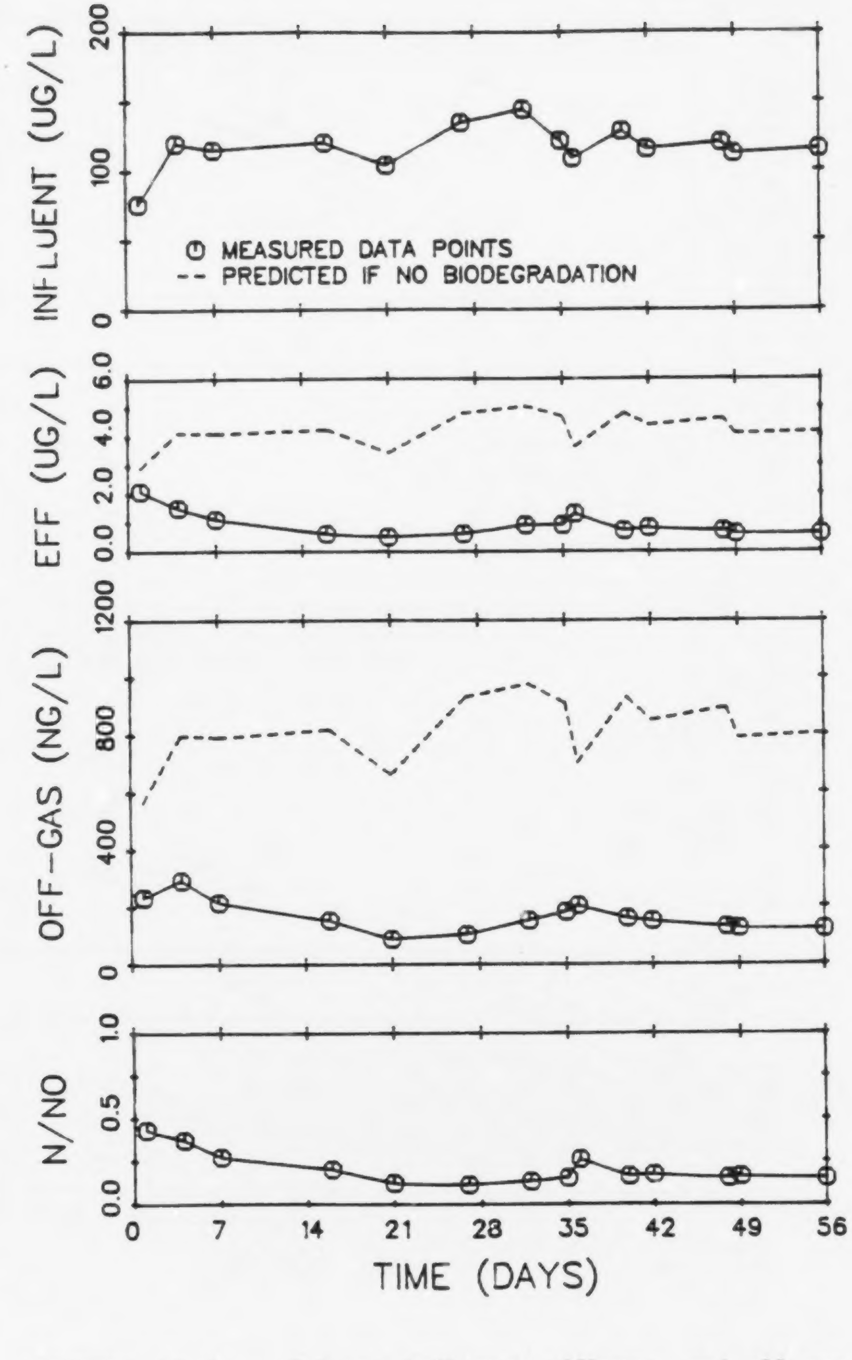


FIGURE 10-34. Toluene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the toluene 6-day SRT activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

TABLE 10-14

SUMMARY OF STEADY-STATE RESULTS FROM THE TOLUENE ACTIVATED SLUDGE BIOREACTOR STUDY CONDUCTED AT A 6-DAY SRT

Parameter	Mean^{+}	Standard Deviation
Influent (μg/ℓ)	119.6	11.6
Effluent (μg/ℓ)	0.8	0.2
Effluent (% of Influent)	0.6	---
Off-Gas (ng/ℓ)	141.7	32.0
Off-Gas (% of Influent)	15.6	---
N/N_o	0.16	0.04
Overall Removal (%)	83.8	---
C_e/C_i	0.006	0.002
Reduction in Aqueous Conc. (%)	99.4	---
Hydraulic Retention Time (hrs.)	5.7	0.2
Aeration Rate (ℓ/min)	4.0	0.1
MLSS (mg/1)	3920	

+ Data Summarized from Days 21 to 56

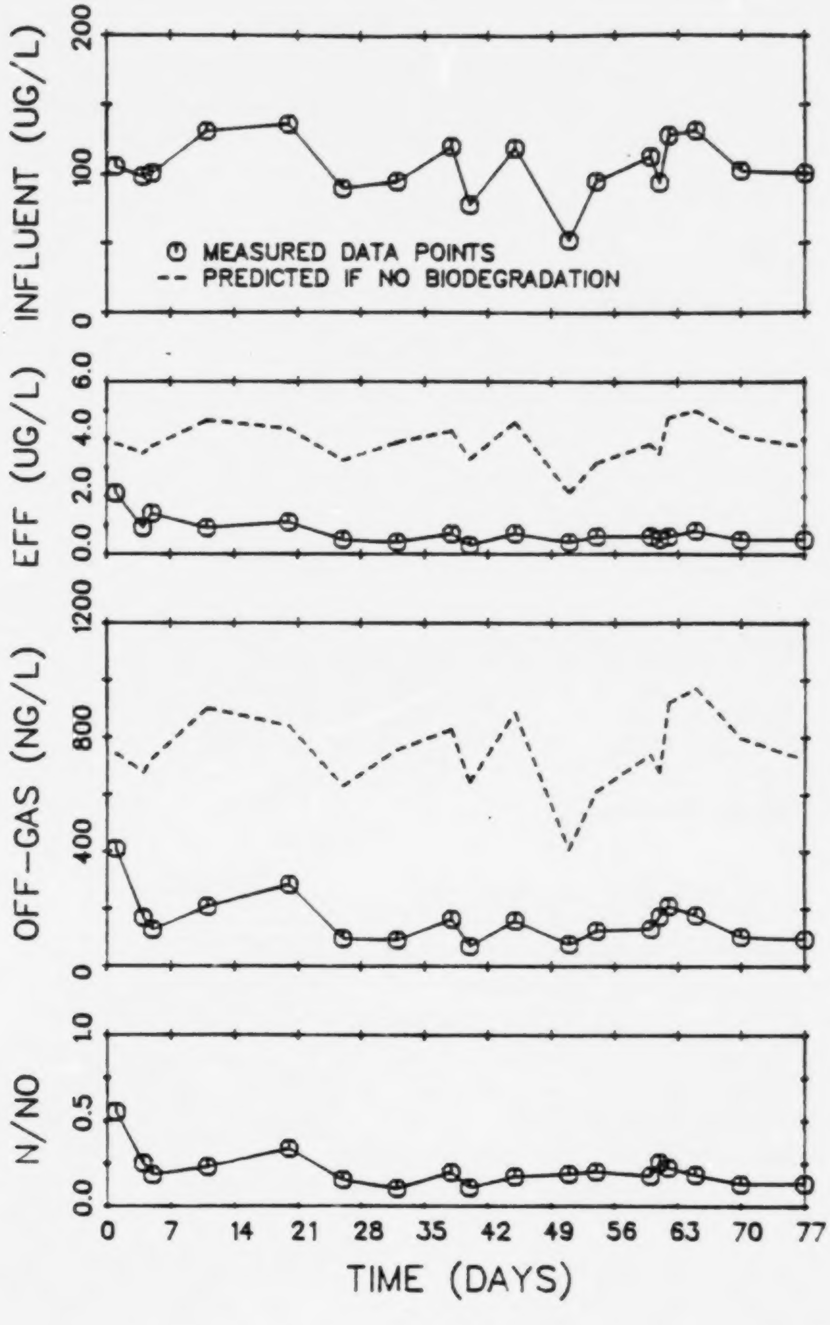


FIGURE 10-35. Toluene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the toluene 12-day SRT activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

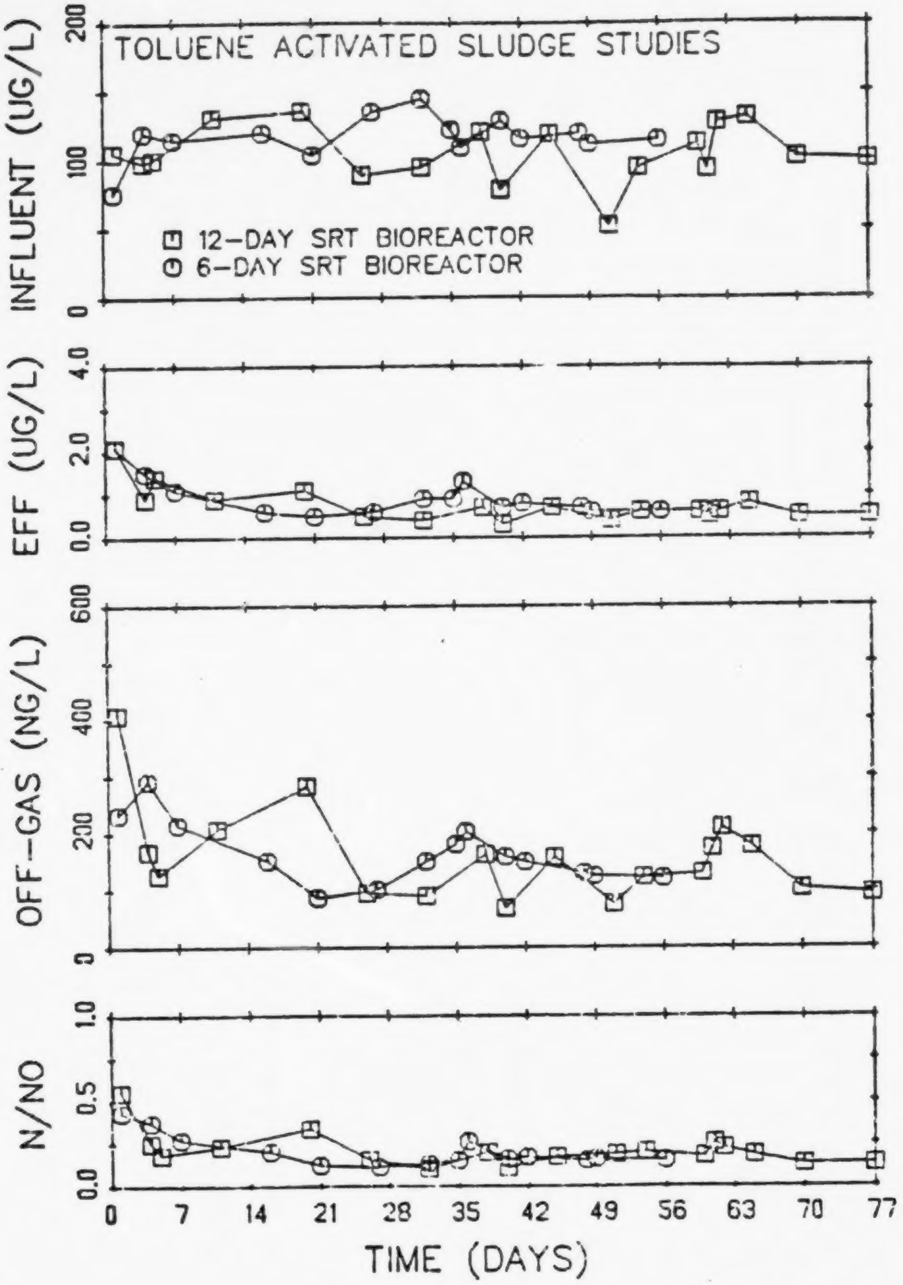


FIGURE 10-36. Comparison of influent, effluent, and off-gas concentrations and fractional recoveries, N/No, from toluene activated sludge studies conducted with 6 and 12-day solids retention times.

TABLE 10-15

COMPARISON OF MEASURED AND PREDICTED EFFLUENT AND OFF-GAS TOLUENE CONCENTRATIONS FROM ACTIVATED SLUDGE BIOREACTORS

	Influent (μg/ℓ)	Effluent (μg/ℓ)	Off-Gas (ng/ℓ)	N/N_o (-)	Removal (%)
6-DAY SRT BIOREACTOR					
Measured	119.6(11.6)	0.8(0.2)	141(32)	0.162(0.04)	83.8(4.0)
Predicted if no biodegradation	--	4.3(0.5)	836(101)	1.00(0.0)	0.0(0.0)
Predicted from effluent	--	--	142(33)	0.162(0.03)	83.8(3.0)
12-DAY SRT BIOREACTOR					
Measured	101.3(21.6)	0.5(0.1)	127(45)	0.170(0.045)	83.0(4.5)
Predicted if no biodegradation	--	3.8(0.5)	737(150)	1.00(0.0)	0.0(0.0)
Predicted from effluent	--	--	106(27)	0.145(0.30)	85.5(3.0)

TABLE 10-16

FATE OF TOLUENE DURING STEADY-STATE BIODEGRADATION BY ACTIVATED SLUDGE

	Percent of Influent Flux	
	6-Day SRT	12-Day SRT
Effluent	0.6	0.5
Off-Gas	15.6	16.5
Biodegraded	83.8	83.0
Days	21-56	26-77

The effect of biodegradation on the fate of toluene is readily apparent in the comparison of measured effluent and off-gas concentrations to the concentrations predicted by the air-stripping model which assumes biodegradation does not occur. Biodegradation effected reductions of 83 and 86% in effluent and off-gas concentrations, respectively, during the steady-state operating period of the 6-day SRT study. Figures 10-37 and 10-38 detail the fate of toluene during the two activated sludge studies by comparing the fraction of the influent flux leaving the bioreactors in effluents and off-gases to the amount removed by biodegradation. During both activated sludge studies the amount of toluene leaving the units in the effluents was extremely small. The most significant effect of biodegradation was the reduction in the mass flux of toluene in the off-gases. Table 10-16 provides a summary of the data plotted in Figures 10-37 and 10-38.

Effluent concentrations were used to predict off-gas concentrations and N/N_0 values, and as indicated by Figures 10-39 and 10-40, the predicted values were generally in good agreement with the measured ones. As effluent concentrations approached the limit of detection for toluene, the ability of the model to predict the off-gas concentrations decreased. The air-stripping model predicted mean off-gas concentrations of 142 and 106 ng/ℓ for the 6 and 12-day SRT studies. Those values were nearly the same as the measured concentrations of 141 and 127 ng/ℓ. Using only measured influent and effluent concentrations, the air-stripping model predicted an overall removal of toluene that was nearly identical to the observed values. Predicted removals averaged 84 and 86% while measured values were 84 and 83% for the 6 and 12-day SRT studies, respectively.

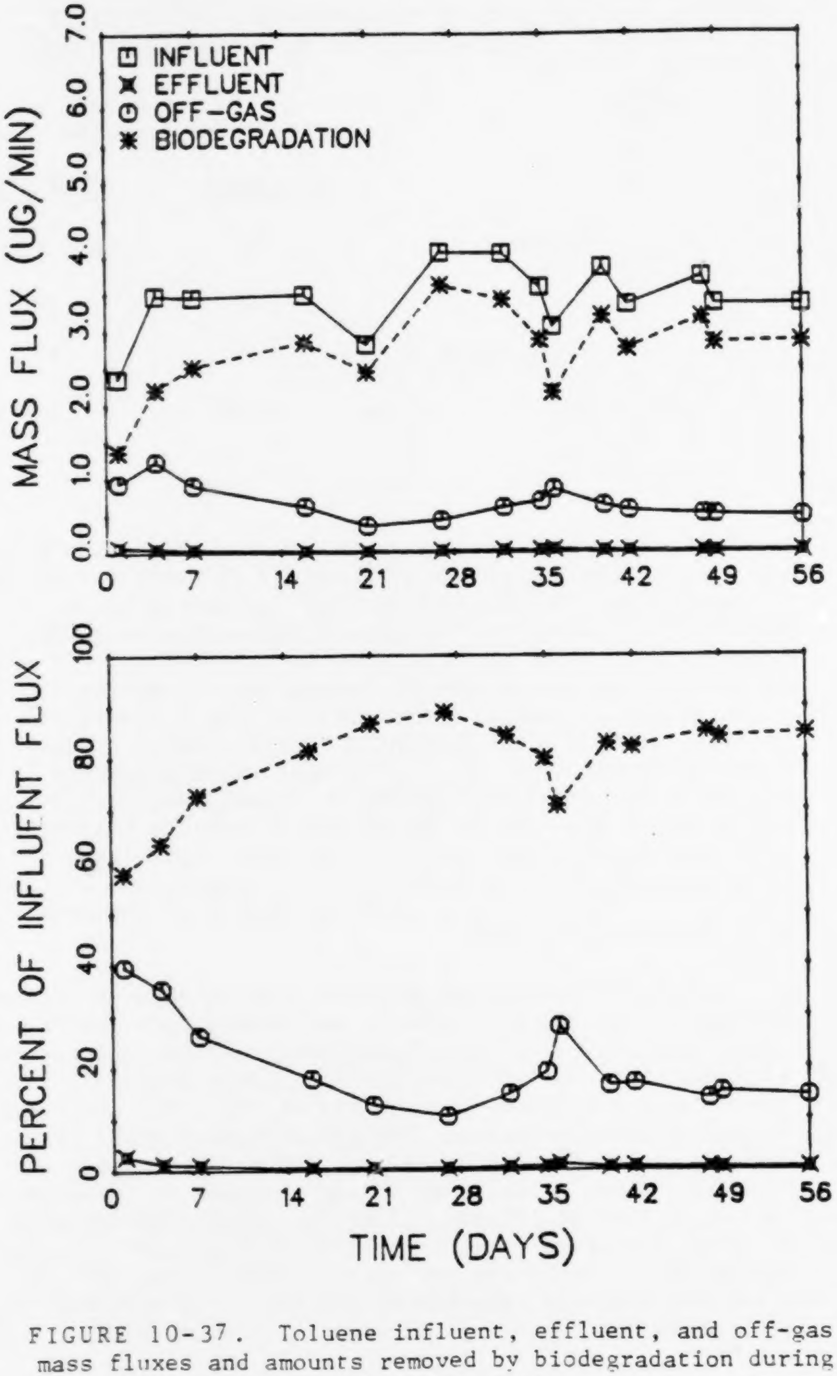


FIGURE 10-37. Toluene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 6-day SRT activated sludge study.

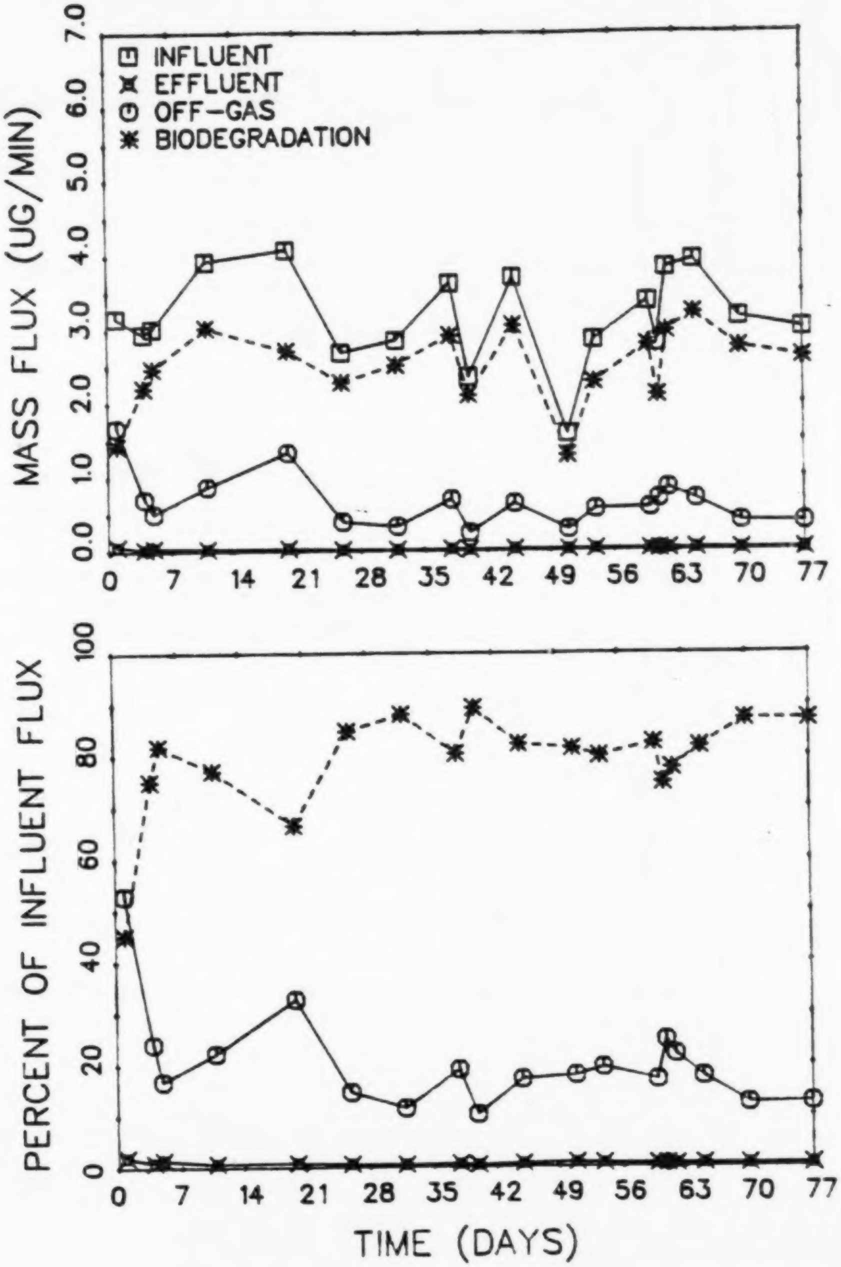


FIGURE 10-38. Toluene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 12-day SRT activated sludge study.

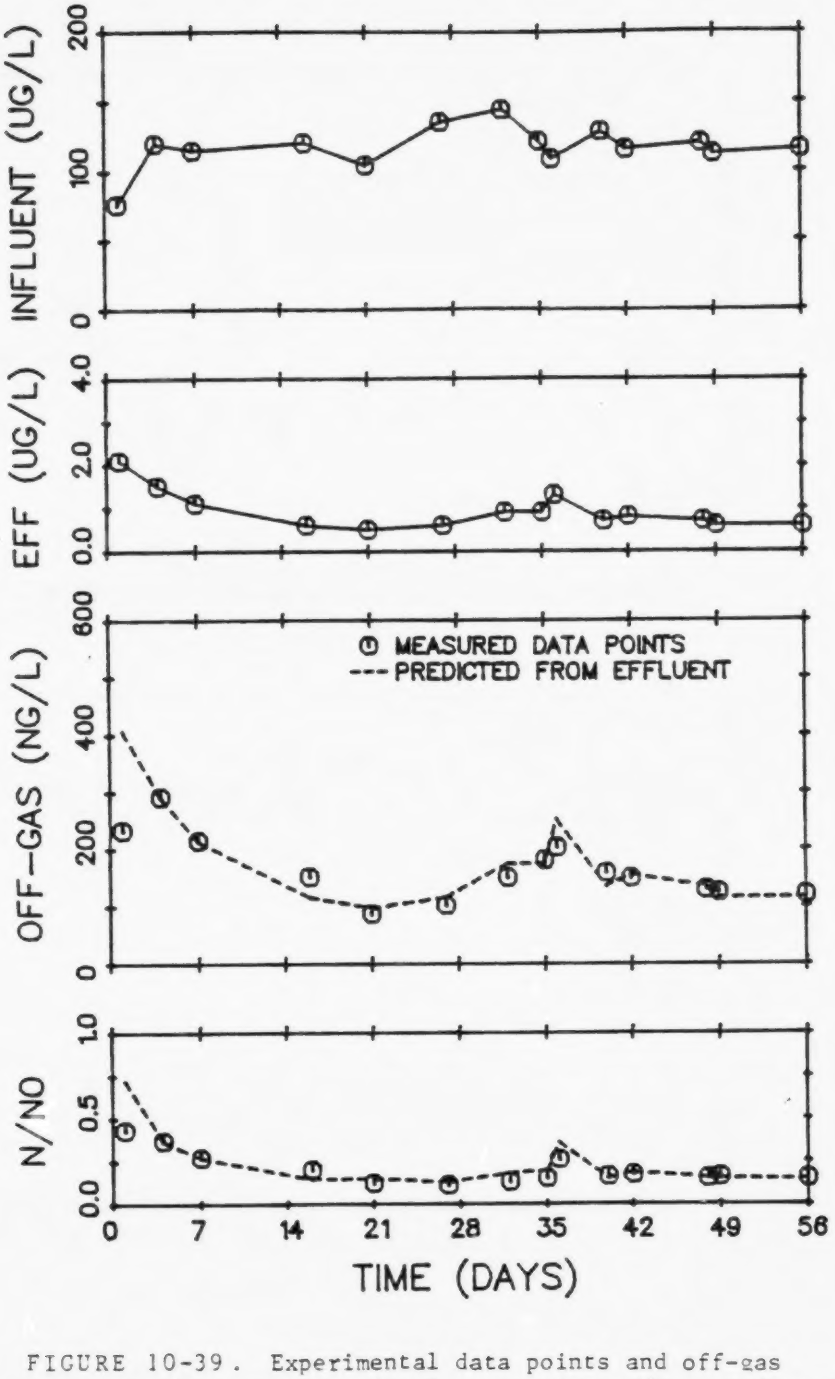


FIGURE 10-39. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 6-day SRT activated sludge study for toluene.

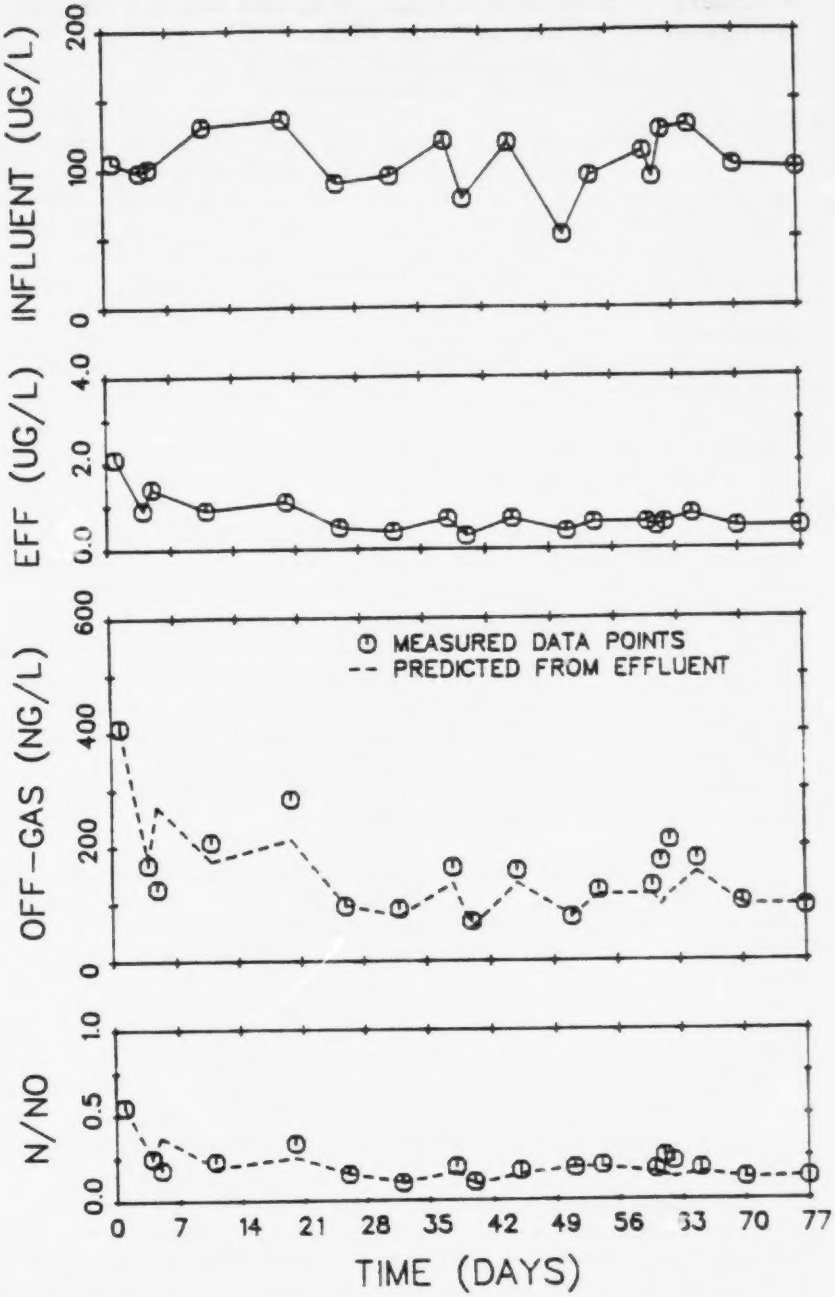


FIGURE 10-40. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concetrations for the 12-day SRT activated sludge study with toluene.

10.4.2.3. Ethylbenzene

Activated sludge studies with ethylbenzene were conducted in 10-liter bioreactors operated with mean solids retention times of 6 and 12 days. Results from the first of two 6-day SRT bioreactor studies are presented in Figures 10-41 and 10-42 (Reactor EB-AS1), and results from the second study, conducted approximately three months later, are given in Figures 10-43 and 10-44 (Reactor EB-AS2). While both activated sludge units experienced similar overall ethylbenzene removals during steady-state operating periods, the reactor performance with respect to ethylbenzene removal during the acclimation periods was significantly different as shown by the comparison of results in Figure 10-45. Steady-state recoveries were achieved between 14 and 21 days in each system and were characterized by mean ethylbenzene removals of 80 and 81% for Reactors EB-AS1 and EB-AS2, respectively.

The acclimation period in Reactor EB-AS2 was similar to those observed for benzene and toluene. Both effluent and off-gas concentrations decreased gradually during the initial two to three weeks resulting in a reduction in the fractional recovery of ethylbenzene, N/N_0, from 0.72 to the steady-state level of 0.19. By contrast, the acclimation period of the activated sludge in Reactor EB-AS1 was characterized by a sharp drop in the effluent and off-gas concentrations between Days 14 and 18. During the first 14 days little change was observed in the effluent and off-gas concentrations, and the fractional recovery ranged between 0.75 and 0.80 indicating only a small amount of ethylbenzene was being biodegraded.

Both reactors were operated under conditions of steady-state ethylbenzene removal for four to five weeks, respectively, during which time effluent and off-gas concentrations remained relatively constant. Effluent and off-gas concentrations averaged 0.5 μg/ℓ and 133 ng/ℓ, during study EB-AS1 and 0.6 μg/ℓ and 166 ng/ℓ during study EB-AS2, respectively. Slight variations in effluent and off-gas concentrations typically reflected changes in the influent concentrations, therefore, the N/N_0 values provided a better representation of the system performance with respect to ethylbenzene removal. The mean N/N_0 values of 0.20 and 0.19 recorded during EB-AS1 and EB-AS2, respectively, indicated the amount of ethylbenzene removed by biodegradation was quite reproducible.

A significant deviation from steady-state conditions occurred in Reactor EB-AS1 on Day 43, as depicted in Figure 10-41, when effluent and off-gas concentrations suddenly increased by a factor of three. The fractional recovery, N/N_0, of ethylbenzene rose to 0.73 on Day 43 compared to the mean steady-state value of 0.20 indicating a significant reduction in biodegradation had occurred. The overall removal of ethylbenzene returned to steady-state levels within two days. Neither a change in TOC removal nor a decrease in the MLSS concentration occurred during this period. The upset which significantly reduced the

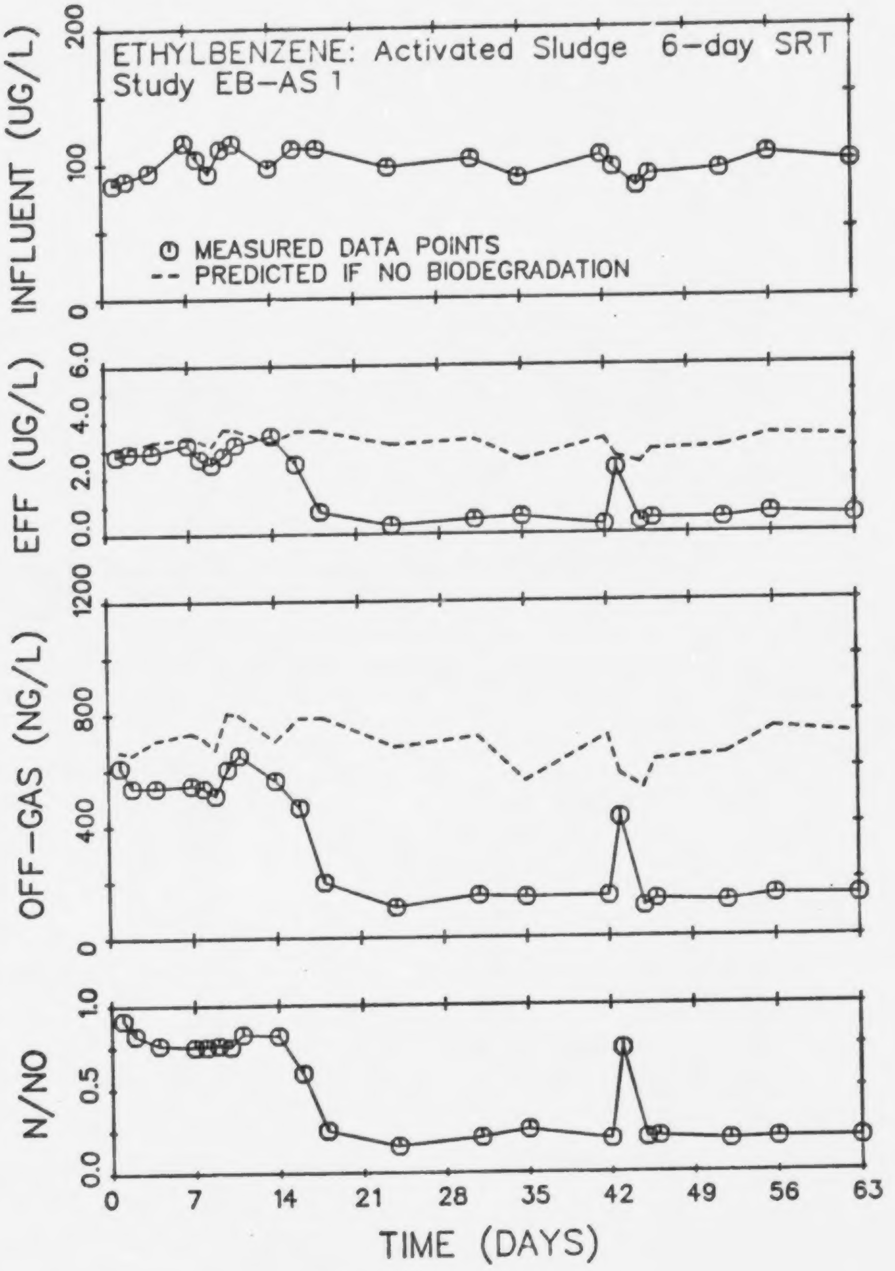


FIGURE 10-41. Ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/N_o, measured during a 6-day SRT ethylbenzene activated sludge study, EB-AS1. (Dashed lines give values predicted to occur in the absence of biodegradation.)

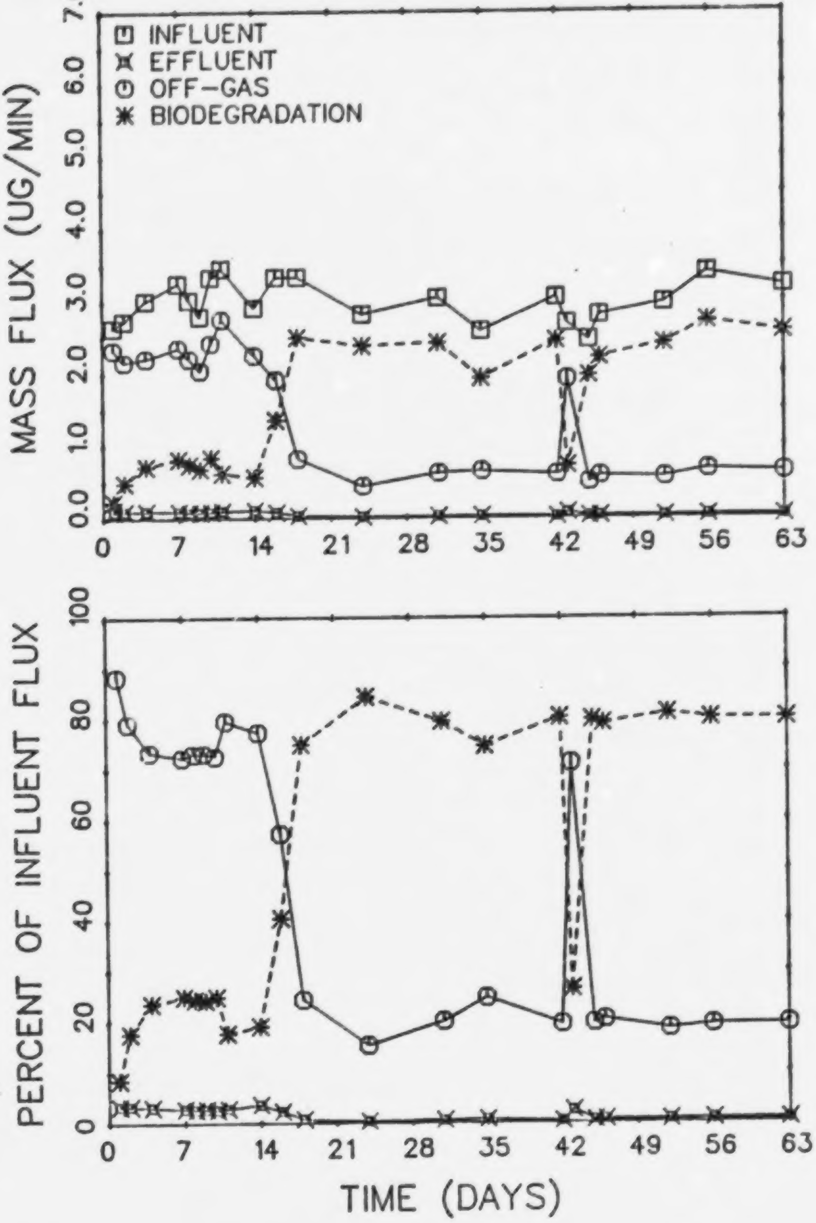


FIGURE 10-42. Ethylbenzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 6-day SRT activated sludge study, EB-AS1.

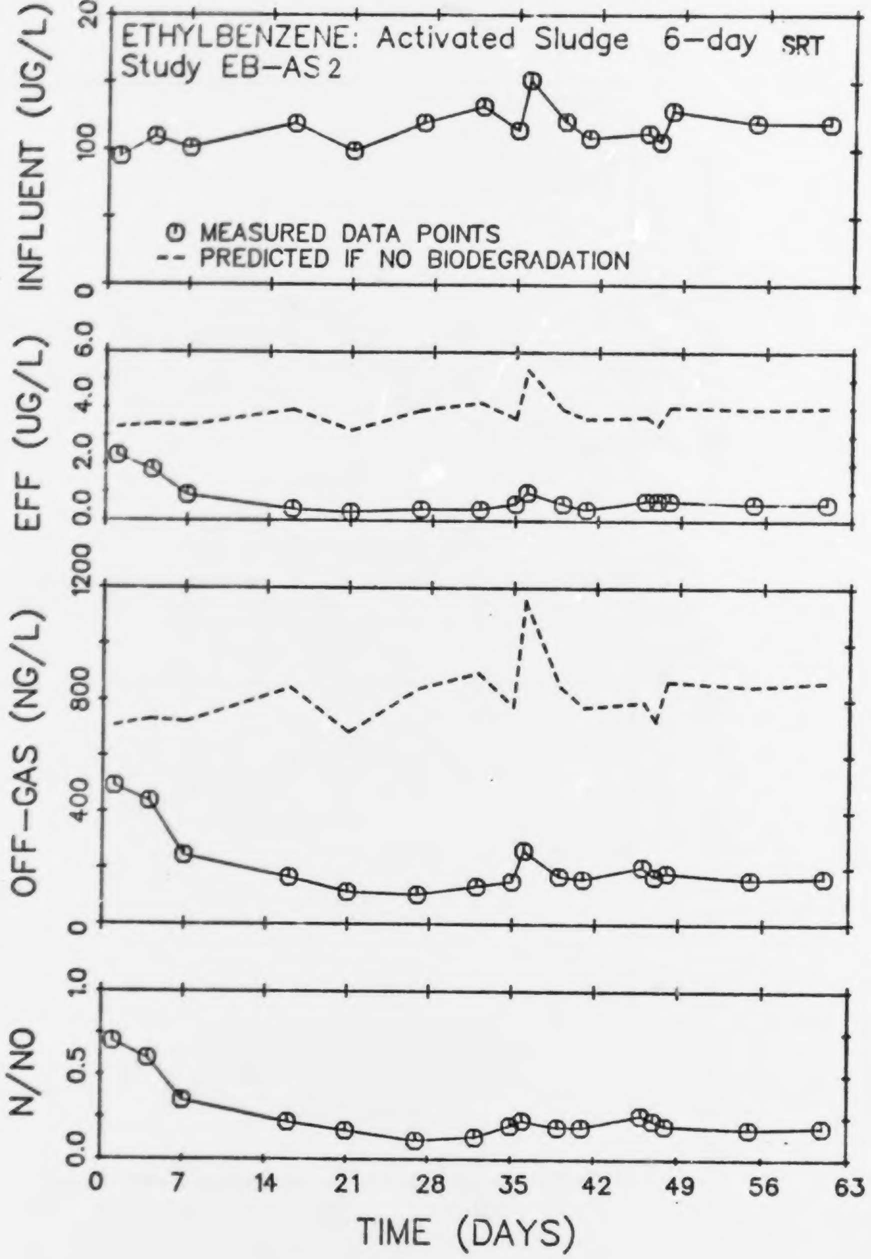


FIGURE 10-43. Ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/N_0, measured during a 6-day SRT ethylbenzene activated sludge study, EB-AS2. (Dashed lines give values predicted to occur in the absence of biodegradation.)

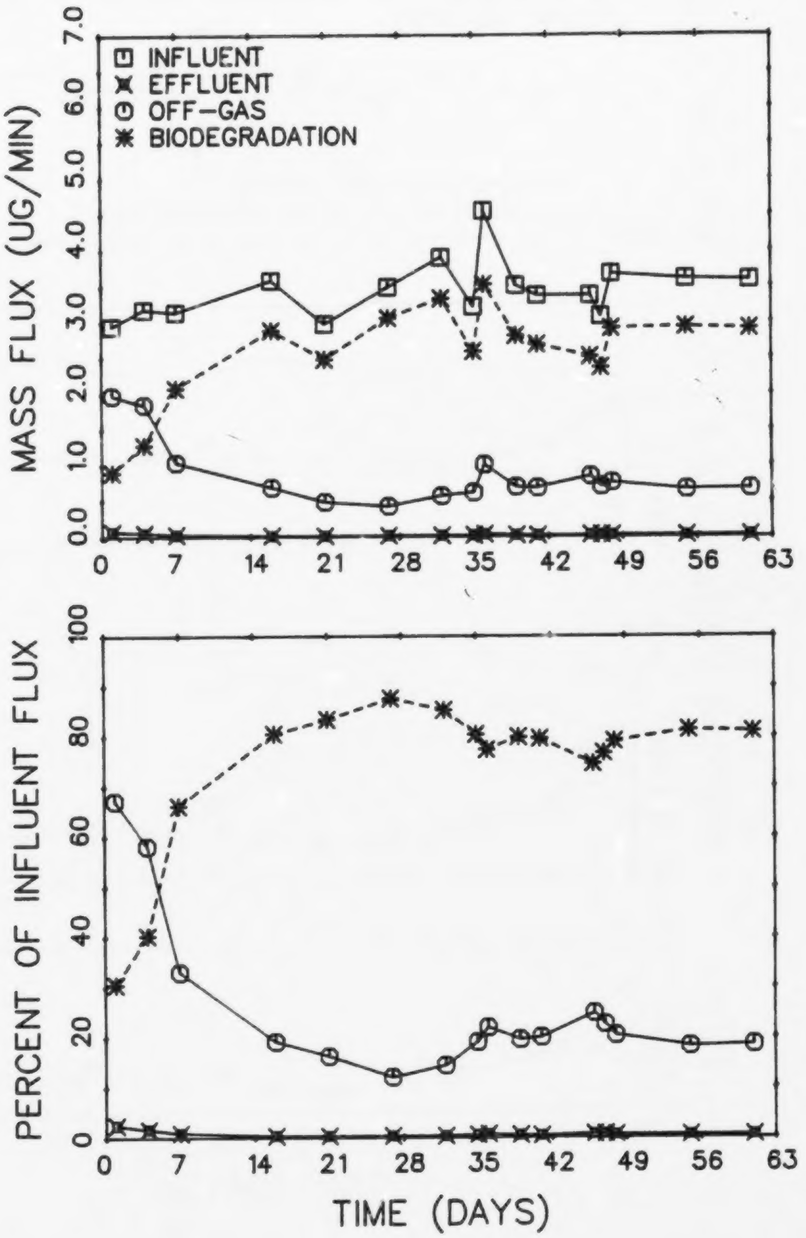


FIGURE 10-44. Ethylbenzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 6-day SRT activated sludge study, EB-AS2.

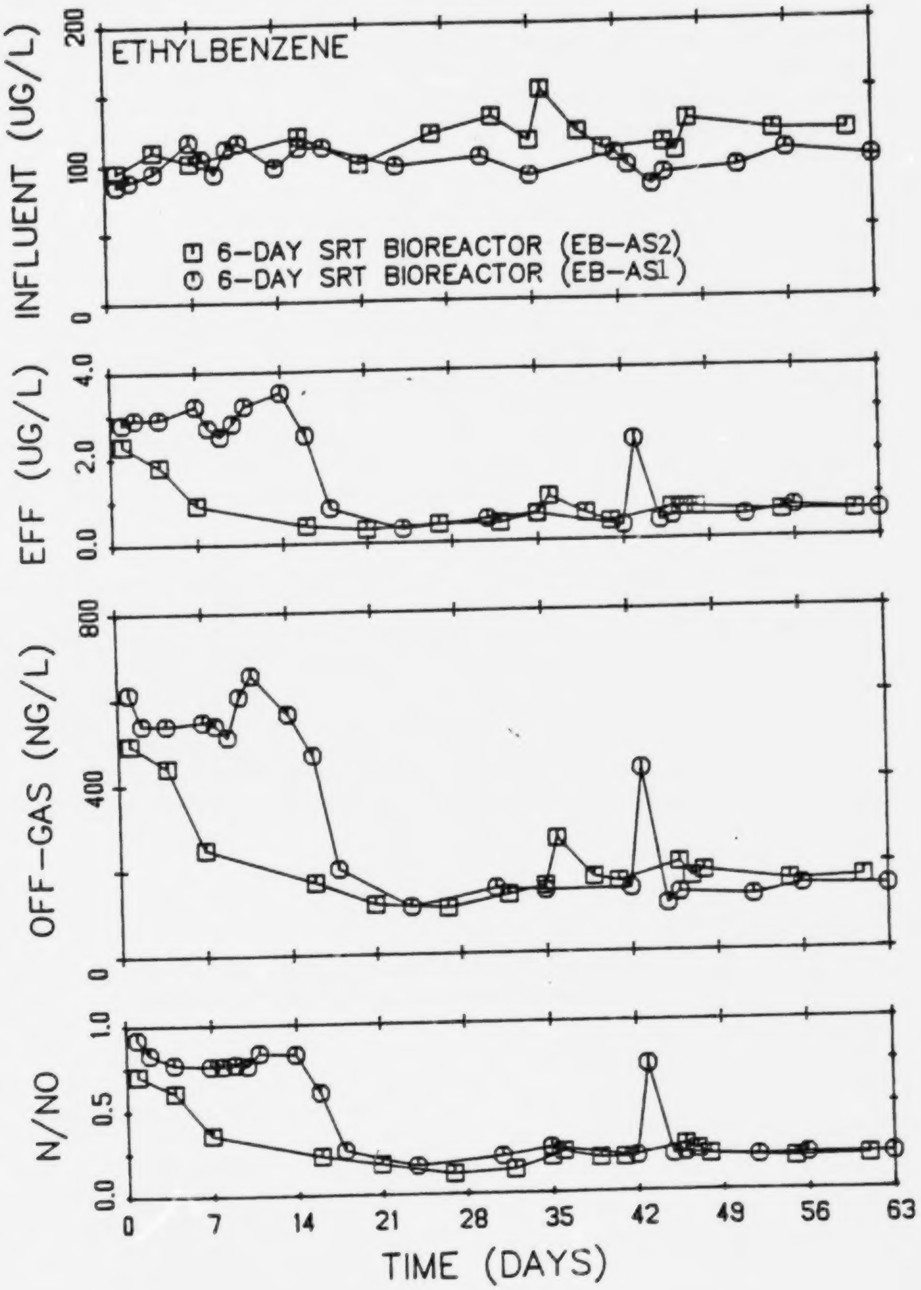


FIGURE 10-45. Comparison of influent, effluent, and off-gas concentrations and fractional recoveries, N/No, from two ethylbenzene activated sludge studies, EB-AS1 and EB-AS2, conducted with 6-day SRT's.

biodegradation rate of ethylbenzene occurred following a temporary drop in the mixed liquor pH from a steady-state value of 7.2 to approximately 6.0 on Day 42. The pH decreased during the night of Day 42 as a result of tubing fatigue within the pumphead of the peristaltic pump delivering buffered ($NaHCO_3$) tap water to reactor EB-AS1. The exact length of time the pH was reduced was estimated to have been less than 12 hours.

Results from an activated sludge bioreactor operated at a 12-day solids retention time are graphically presented in Figures 10-46 and 10-47. Significant biodegradation was evidenced by the fact that the effluent and off-gas concentrations were less than the values predicted to occur by the air stripping model if ethylbenzene was not removed by biodegradation. As shown by the comparison of results from the 6 and 12-day SRT activated sludge studies in Figure 10-48, no variation in effluent and off-gas concentrations or amounts biodegraded was observed at the two SRT's studied. Overall removals of ethylbenzene, during approximately five weeks of steady-state conditions, averaged 81% in the 6-day SRT study (Reactor EB-AS2) compared with 82% in the 12-day SRT study.

The overall removals of ethylbenzene due to biodegradation during the two 6-day SRT studies and the 12-day SRT study have been compared by the plots in Figure 10-49. Following the two to three week acclimation phase there was no significant difference in the amount of ethylbenzene biodegraded. The amount of ethylbenzene removed by biodegradation averaged 81% for the three activated sludge studies. The amount of ethylbenzene in the off-gases and effluents averaged 18.5% and 0.5%, respectively. Table 10-17 summarizes the fate of ethylbenzene during activated sludge treatment in the experimental system.

TABLE 10-17

FATE OF ETHYLBENZENE DURING STEADY-STATE
BIODEGRADATION BY ACTIVATED SLUDGE

	Percent of Influent Flux		
	6-Day SRT (EB-AS1)	6-Day SRT (EB-AS2)	12-Day SRT
Effluent	0.5	0.5	0.5
Off-Gas	19.5	18.5	17.5
Biodegraded	80	81	82
Biosorbed	0	0	0
Days	21-42,45-63	21-63	21-52,58-70

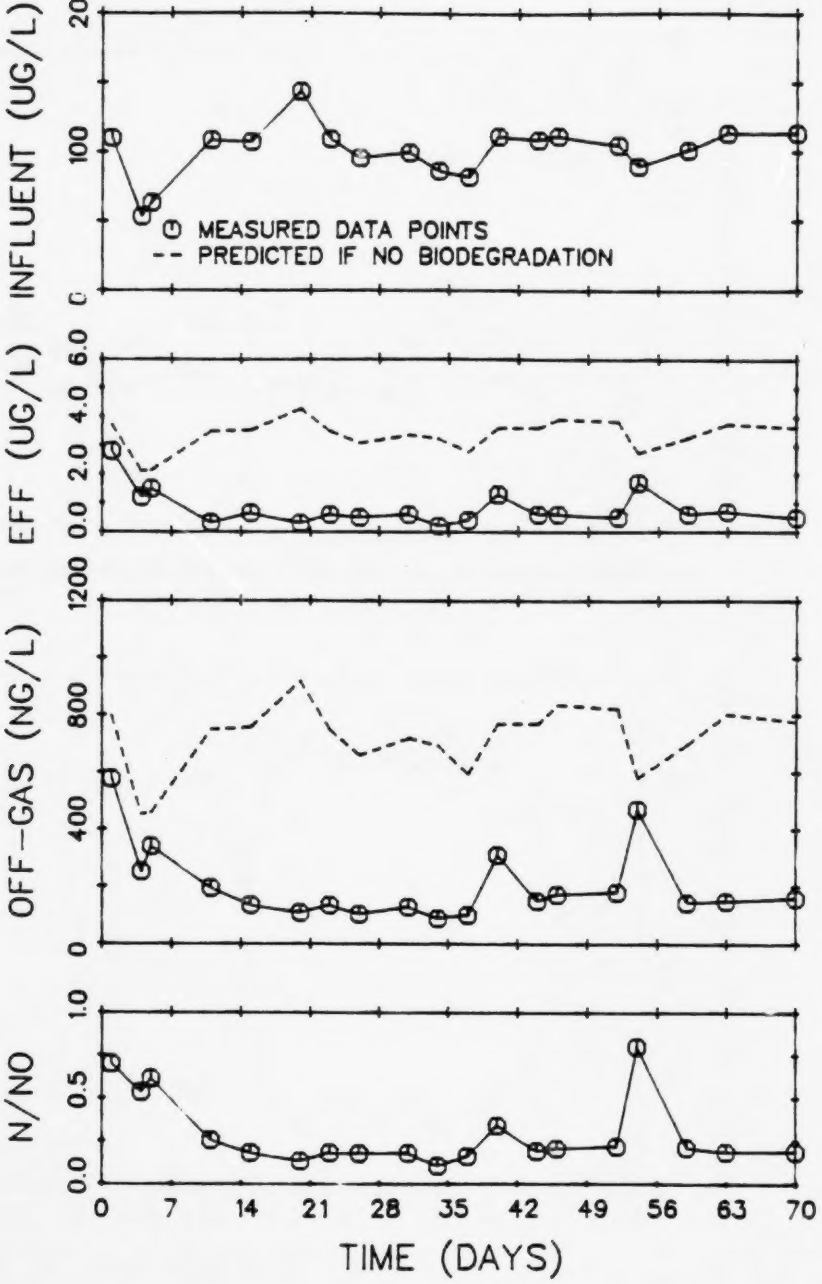


FIGURE 10-46. Ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the 12-day SRT activated sludge study. (dashed lines give values predicted to occur in the absence of biodegradation.)

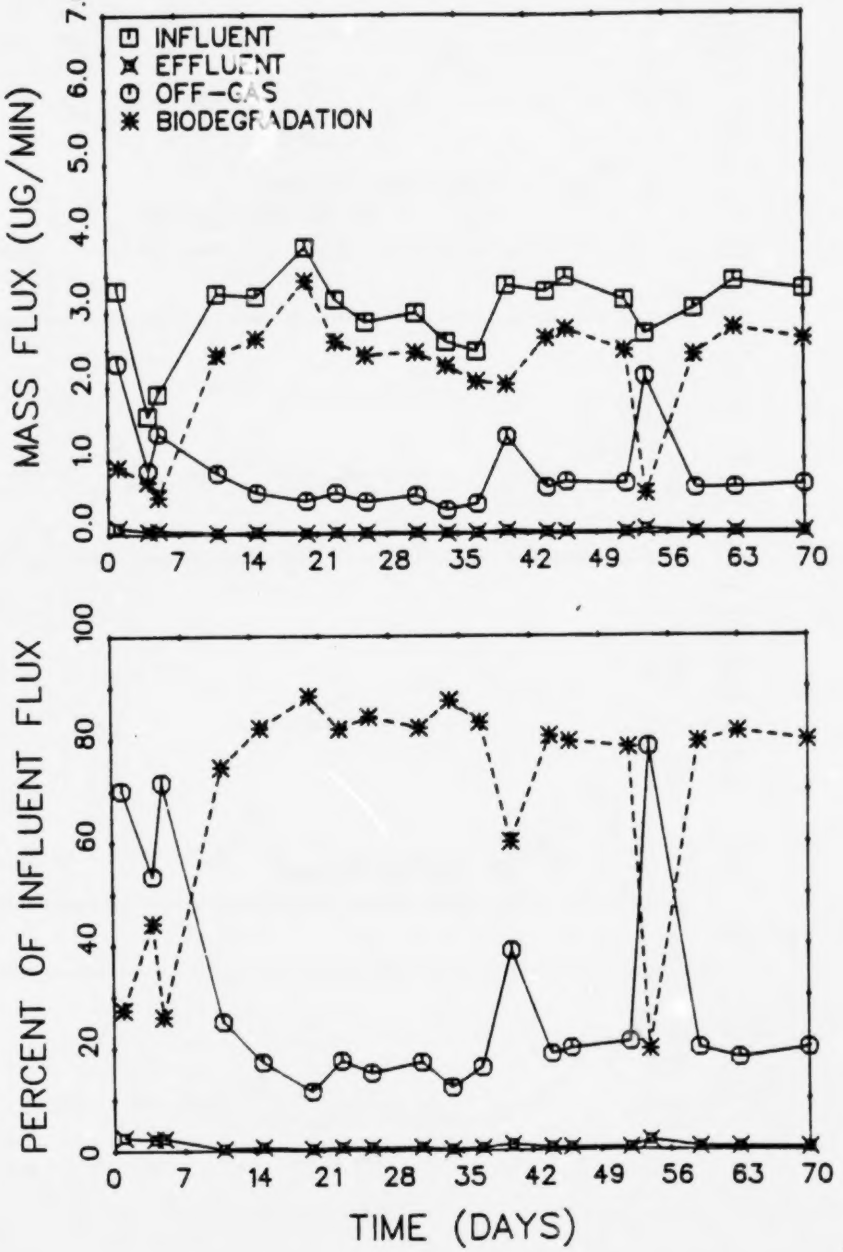


FIGURE 10-47. Ethylbenzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 12-day SRT ethylbenzene activated sludge study.

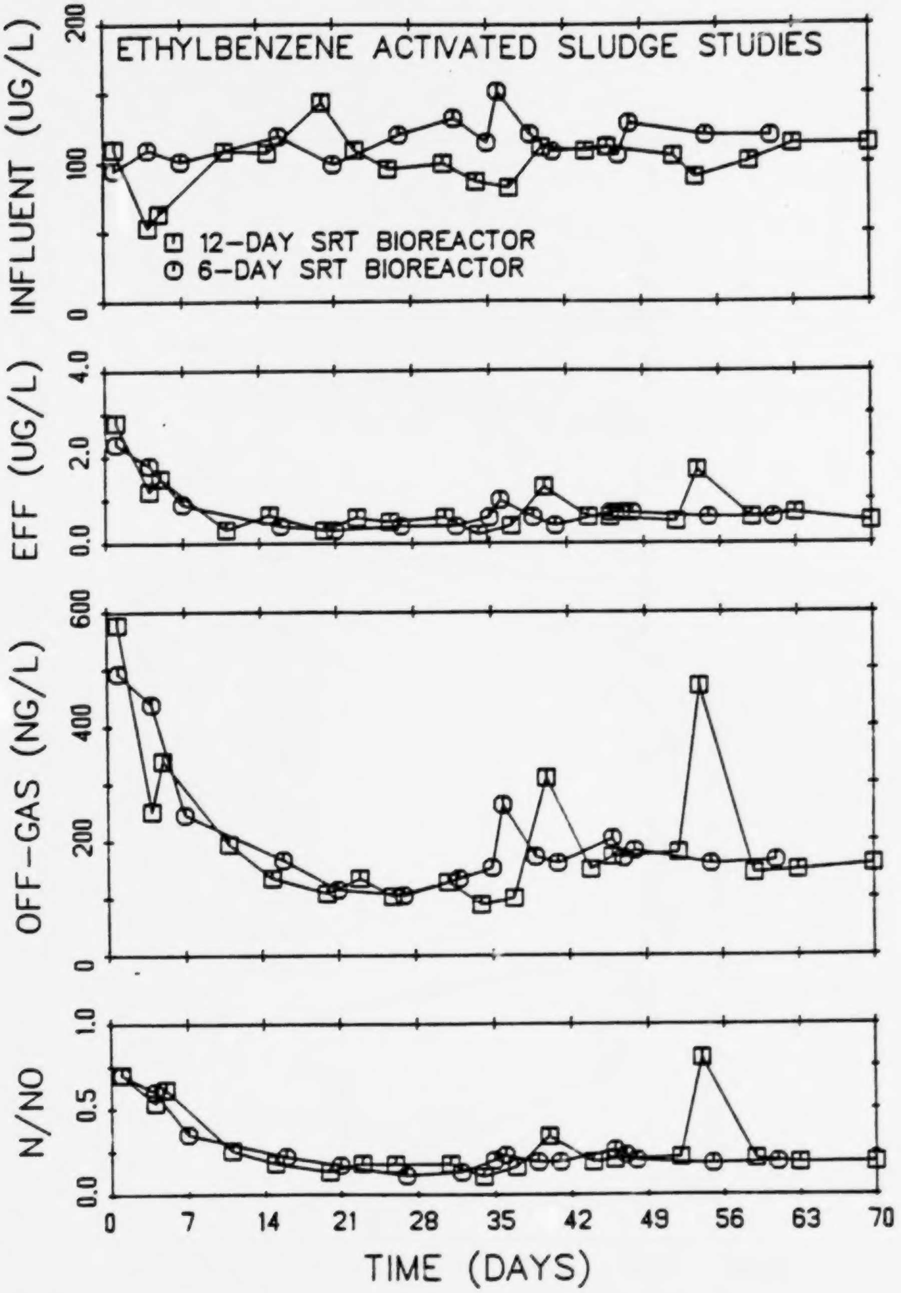


FIGURE 10-48. Comparison of influent, effluent, and off-gas concentrations and fractional recoveries. N/No, from ethylbenzene activated sludge studies conducted with 6 (EB-AS2) and 12-day SRT's.

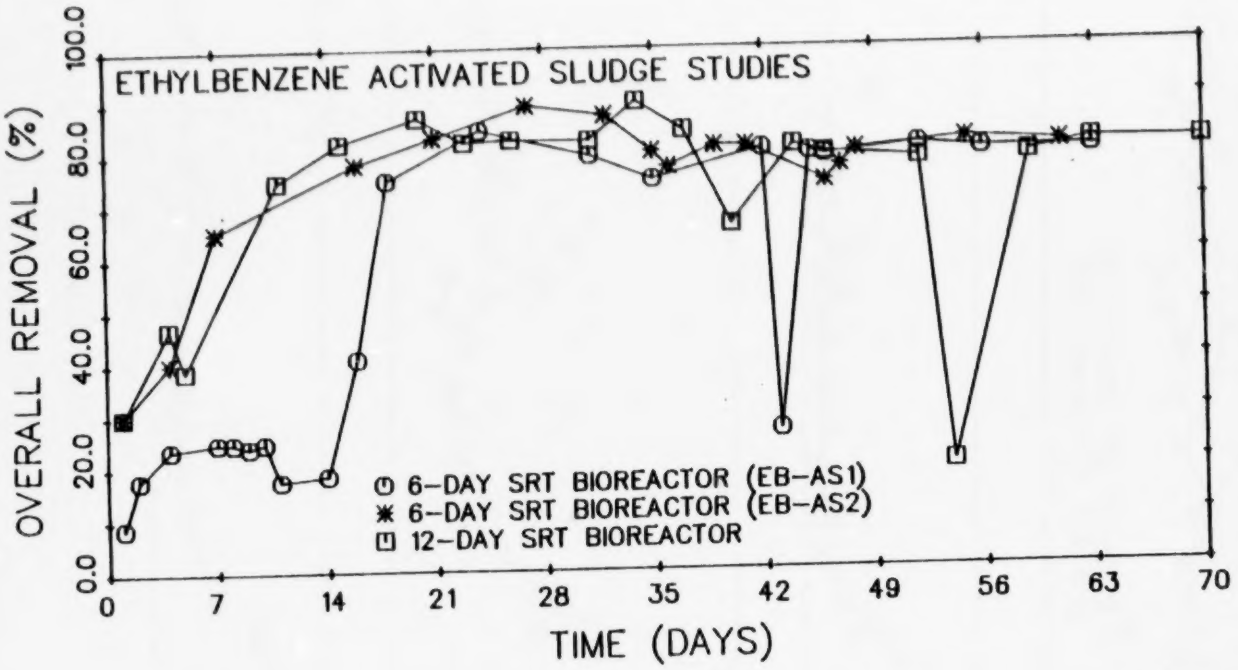


FIGURE 10-49. Overall ethylbenzene removals due to biodegradation measured during activated sludge studies conducted in 10-liter bioreactors operated with 6 and 12-day solids retention times.

Volatilization of ethylbenzene was sufficiently characterized in the 10-liter bioreactors to enable predictions of off-gases and overall removals based upon measured effluent concentrations, as was shown for the previous compounds and is demonstrated for ethylbenzene in Figures 10-50, 10-51 and 10-52. In general, there was good agreement between predicted and measured off-gas concentrations and N/N_0 values for the three ethylbenzene activated sludge bioreactor studies. The predicted off-gas concentrations were typically slightly less than the measured concentrations in each study. Ratios of predicted:measured average off-gas concentrations ranged from 0.76 to 0.81 for the three activated sludge studies. The smaller predicted values likely resulted from effluent concentrations that consistently were less than 1.0 μg/ℓ and approached the limit of detection for ethylbenzene. Amounts of ethylbenzene removed by biodegradation and hence not leaving the reactors were quite well modeled from the effluent analyses. Ratios of predicted:measured percent overall removals were approximately 1.05 in each study. The larger than measured removals resulted from the model predicting less flux out of the bioreactors in the off-gas than was actually observed.

A complete summary of the activated sludge bioreactor data for ethylbenzene is given in Table 10-18. The results include measured influent, effluent, and off-gas concentrations; effluent and off-gas concentrations predicted to occur if only air-stripping effected a reduction in the aqueous ethylbenzene concentration; and off gas concentrations predicted from measured effluent values. The mean values were calculated for conditions of steady-state ethylbenzene removal and do not include either acclimation periods or upset periods resulting in reduced ethylbenzene biodegradation.

10.4.2.4 O-Xylene

Activated sludge bioreactor studies with o-xylene were conducted at solids retention times of 6 and 12-days. Two activated sludge bioreactor studies were conducted with 6-day SRT's and results from the first study (XYL-AS1) are given in Figures 10-53 and 10-54 while results from the second study (XYL-AS2) conducted six months later are given in Figures 10-55 and 10-56. Biodegradation of o-xylene by the activated sludge was observed in both studies and was evidenced by significant differences between measured mass fluxes into (influent) and out of (effluent, off-gas and waste sludge combined) the bioreactors. The dashed lines in Figures 10-53 and 10-55 represent the amount of o-xylene predicted by the air-stripping model to occur in effluents and off-gases if only air-stripping effected a reduction in the aqueous concentrations. Differences between the measured data points and dashed lines represent reductions in effluent and off-gas concentrations due to microbial degradation of o-xylene. Both activated sludge units experienced similar o-xylene removals during steady-state operating periods as shown by the comparison of results from the two studies in Figure 10-57. Steady-state removals in each bioreactor were achieved after approximately three weeks and were characterized by mean o-xylene

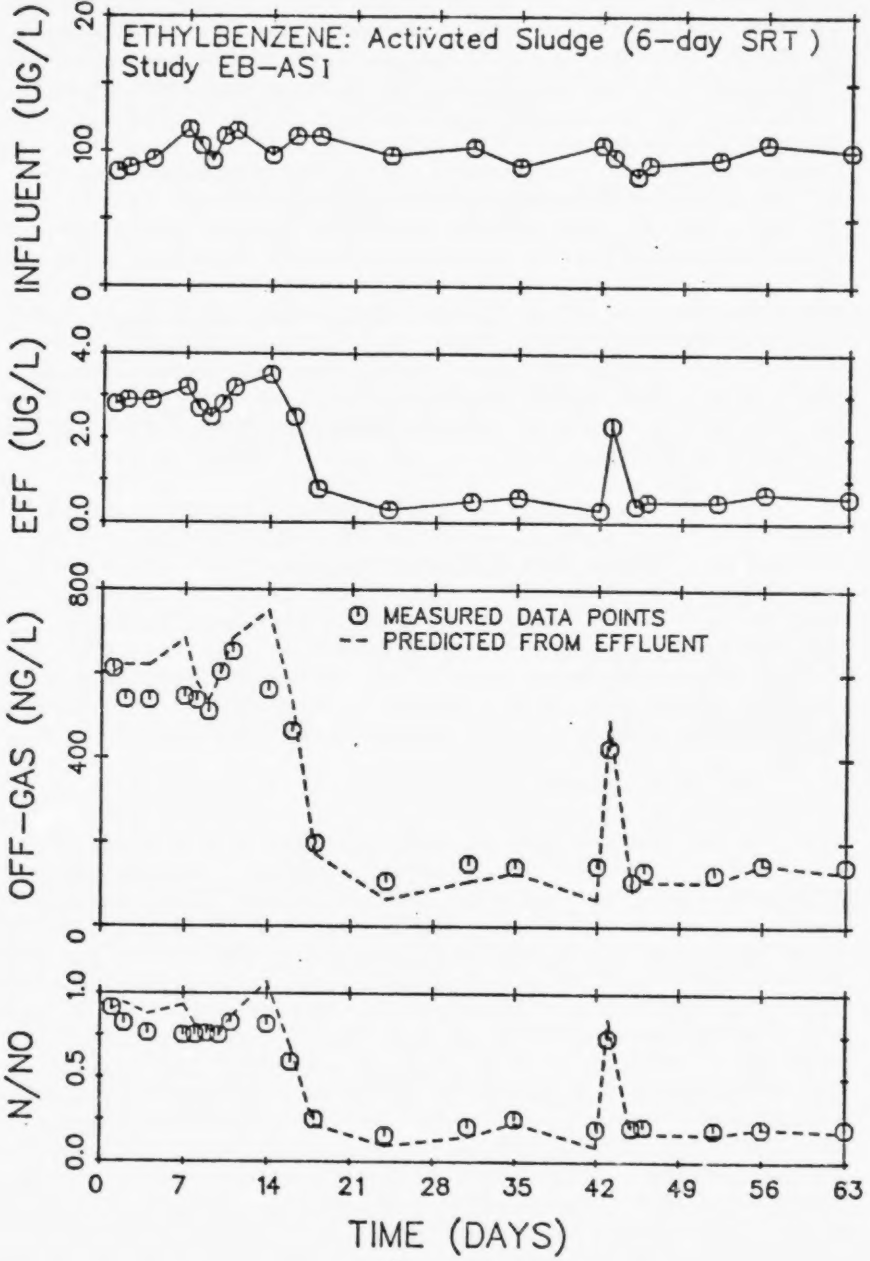


FIGURE 10-50. Experimental data points and off-gas concentrations and fractional recoveries, N/N_0, predicted from measured effluent concentrations for the 6-day SRT activated sludge study with ethylbenzene, EB-AS1.

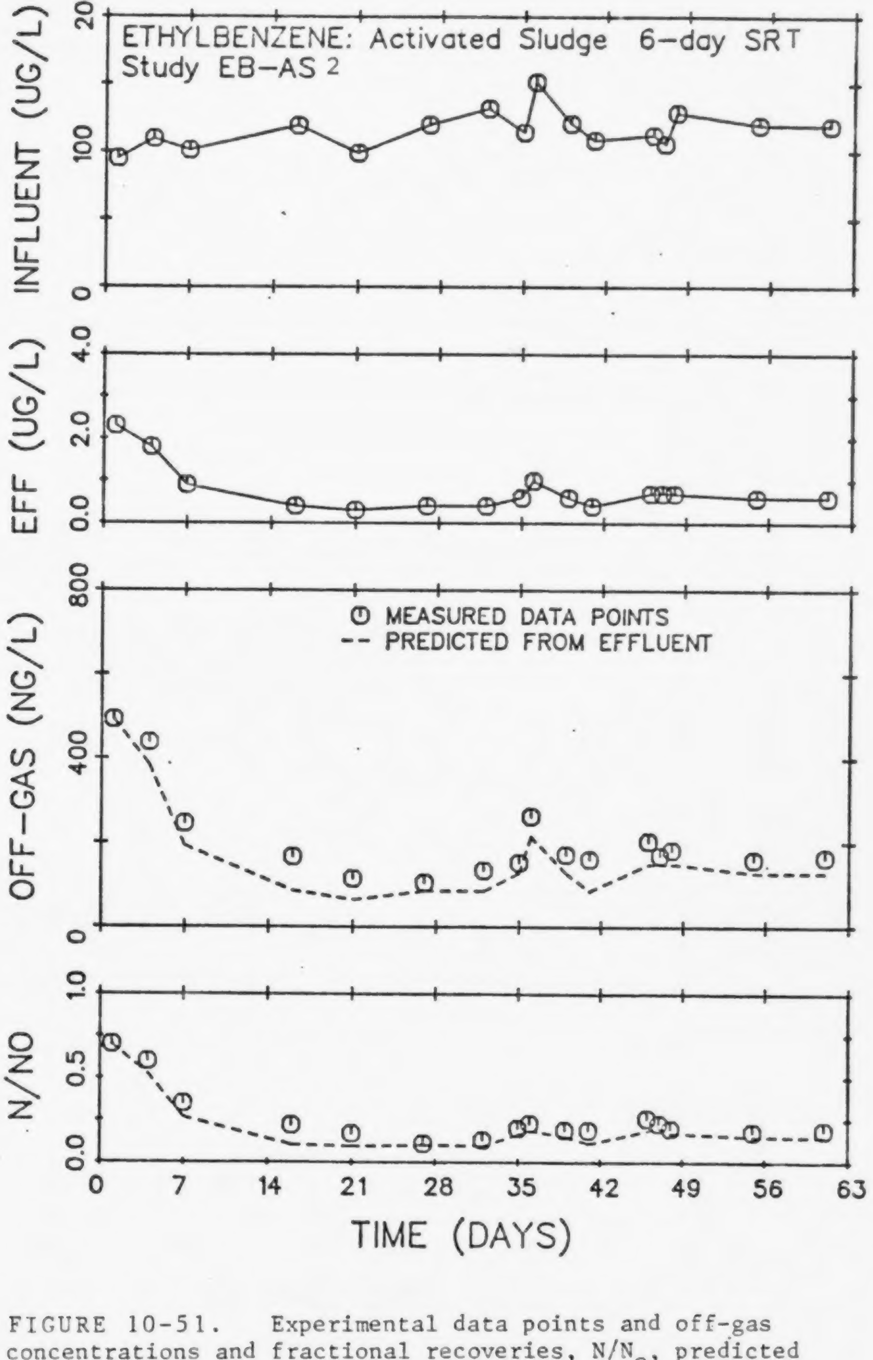


FIGURE 10-51. Experimental data points and off-gas concentrations and fractional recoveries, N/N_0, predicted from measured effluent concentrations for the 6-day SRT activated sludge study with ethylbenzene, EB-AS2.

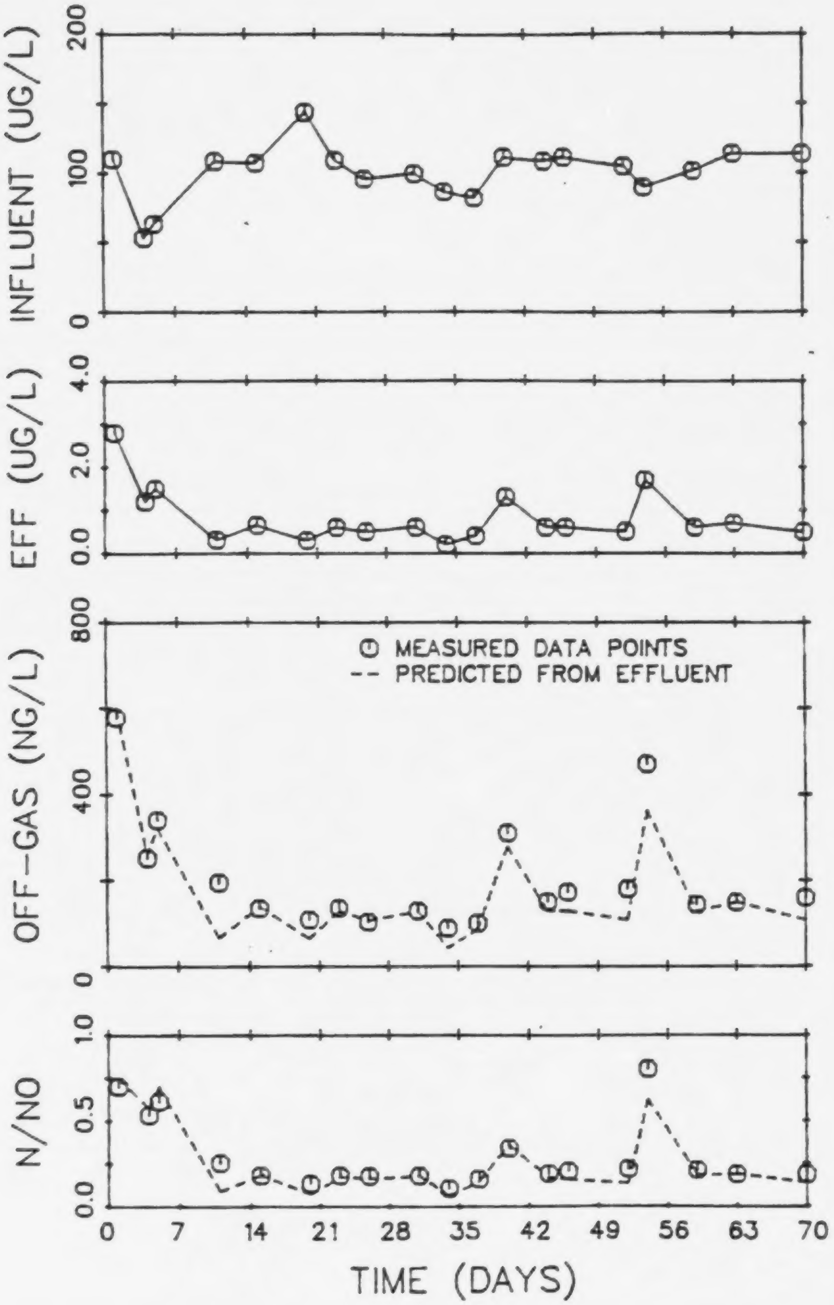


FIGURE 10-52. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 12-day SRT activated sludge study with ethylbenzene.

TABLE 10-18

COMPARISON OF MEASURED AND PREDICTED EFFLUENT AND OFF-GAS ETHYLBENZENE CONCENTRATIONS FROM ACTIVATED SLUDGE BIOREACTORS

	Influent (μg/ℓ)	Effluent (μg/ℓ)	Off-Gas (ng/ℓ)	N/N_o (-)	Removal (%)
		6-DAY SRT; REACTOR EB-AS1			
Measured	97.6(8.5)	0.5(0.1)	133(17)	0.20(0.02)	80(2)
Predicted if no biodegradation	--	3.1(0.4)	653(76)	1.00(0.0)	0(0)
Predicted from effluent	--	--	111(34)	0.17(0.05)	83(5)
		6-DAY SRT; REACTOR EB-AS2			
Measured	119.4(14.4)	0.6(0.2)	166(43)	0.19(0.04)	81(4)
Predicted if no biodegradation	--	4.0(0.5)	850(121)	1.00(0.0)	0(0)
Predicted from effluent	--	--	125(43)	0.15(0.04)	85(4)
		12-DAY SRT			
Measured	105.2	0.5(0.1)	135(30)	0.18(0.03)	82(3)
Predicted if no biodegradation	--	3.5(0.4)	756(80)	1.00(0.0)	0(0)
Predicted from effluent	--	--	110(30)	0.15(0.04)	85(4)

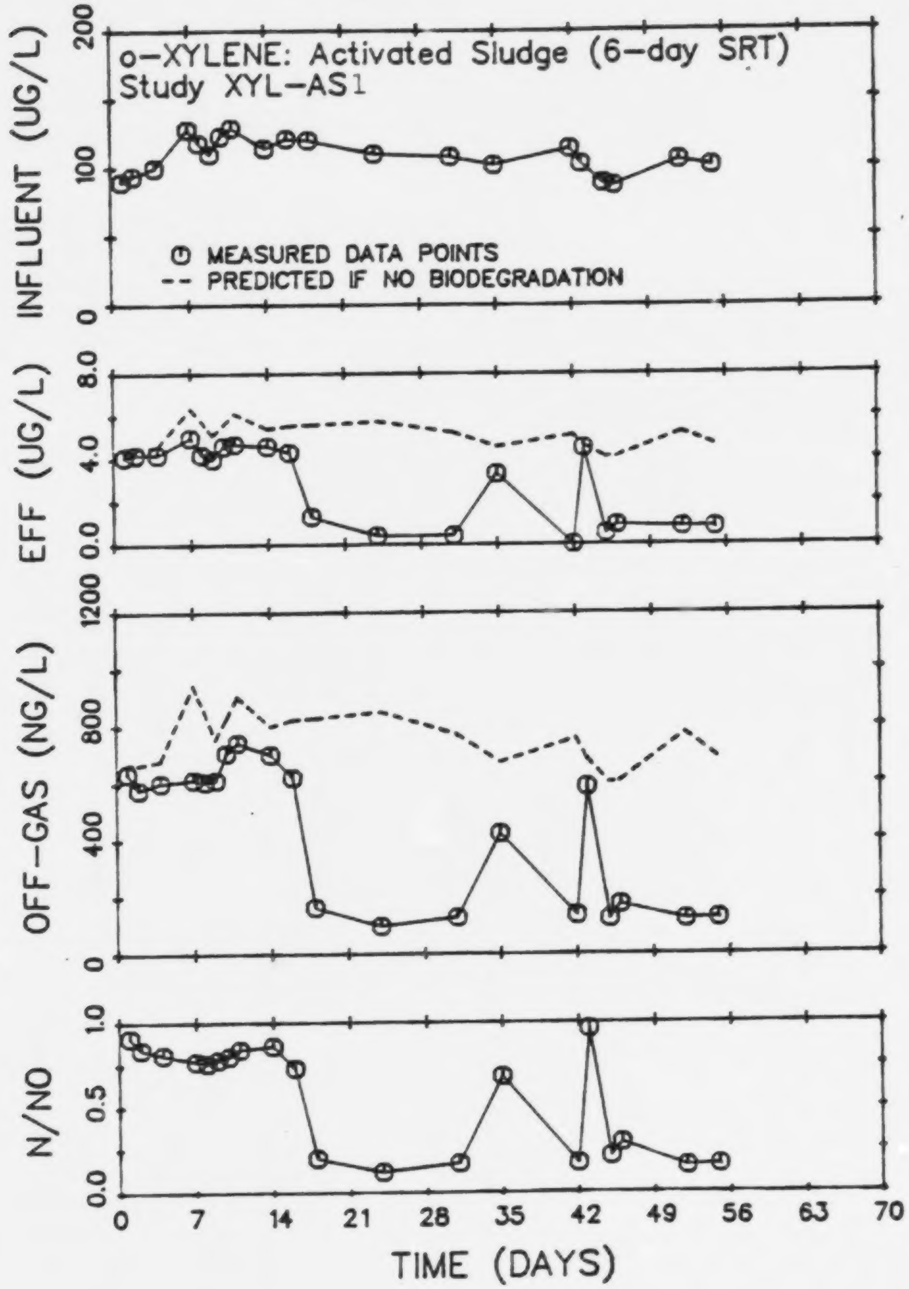


FIGURE 10-53. o-Xylene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during a 6-day SRT o-xylene activated sludge study, XYL-AS1. (Dashed lines give values predicted to occur in the absence of biodegradation.)

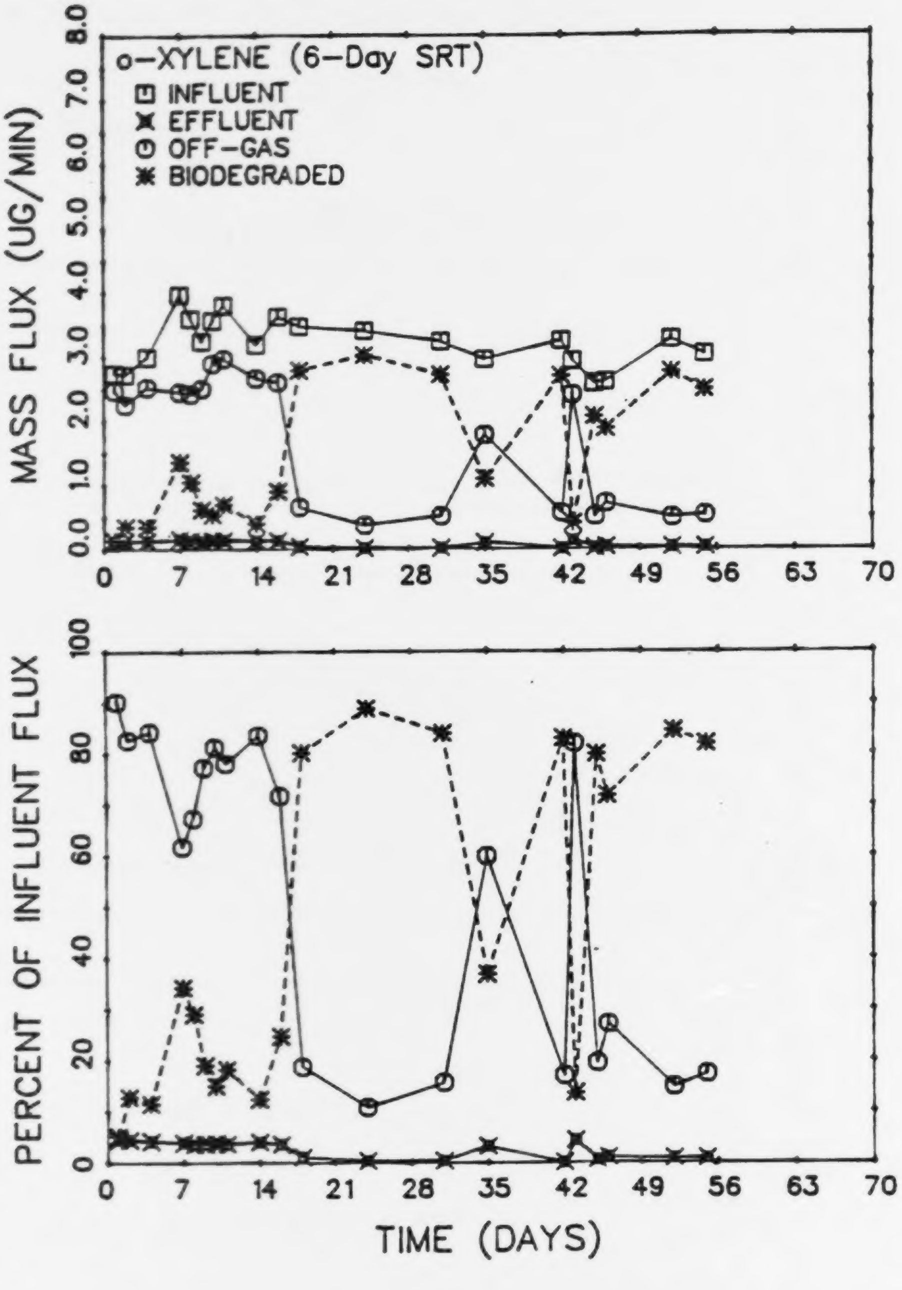


FIGURE 10-54. o-Xylene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 6-day SRT o-xylene activated sludge study, XYL-AS1.

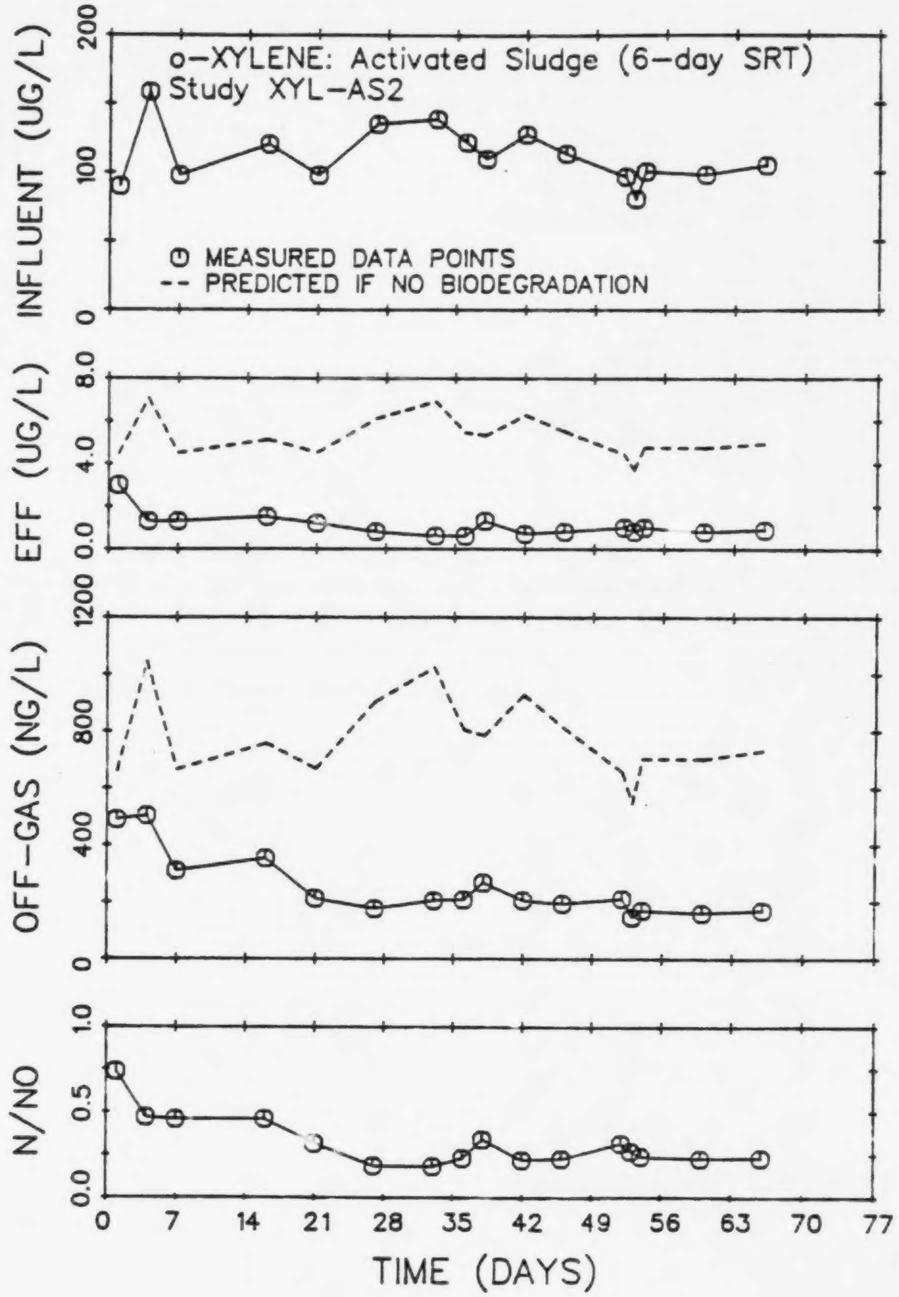


FIGURE 10-55. o-Xylene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during a 6-day SRT o-xylene activated sludge study, XYL-AS2. (Dashed lines give values predicted to occur in the absence of biodegradation.)

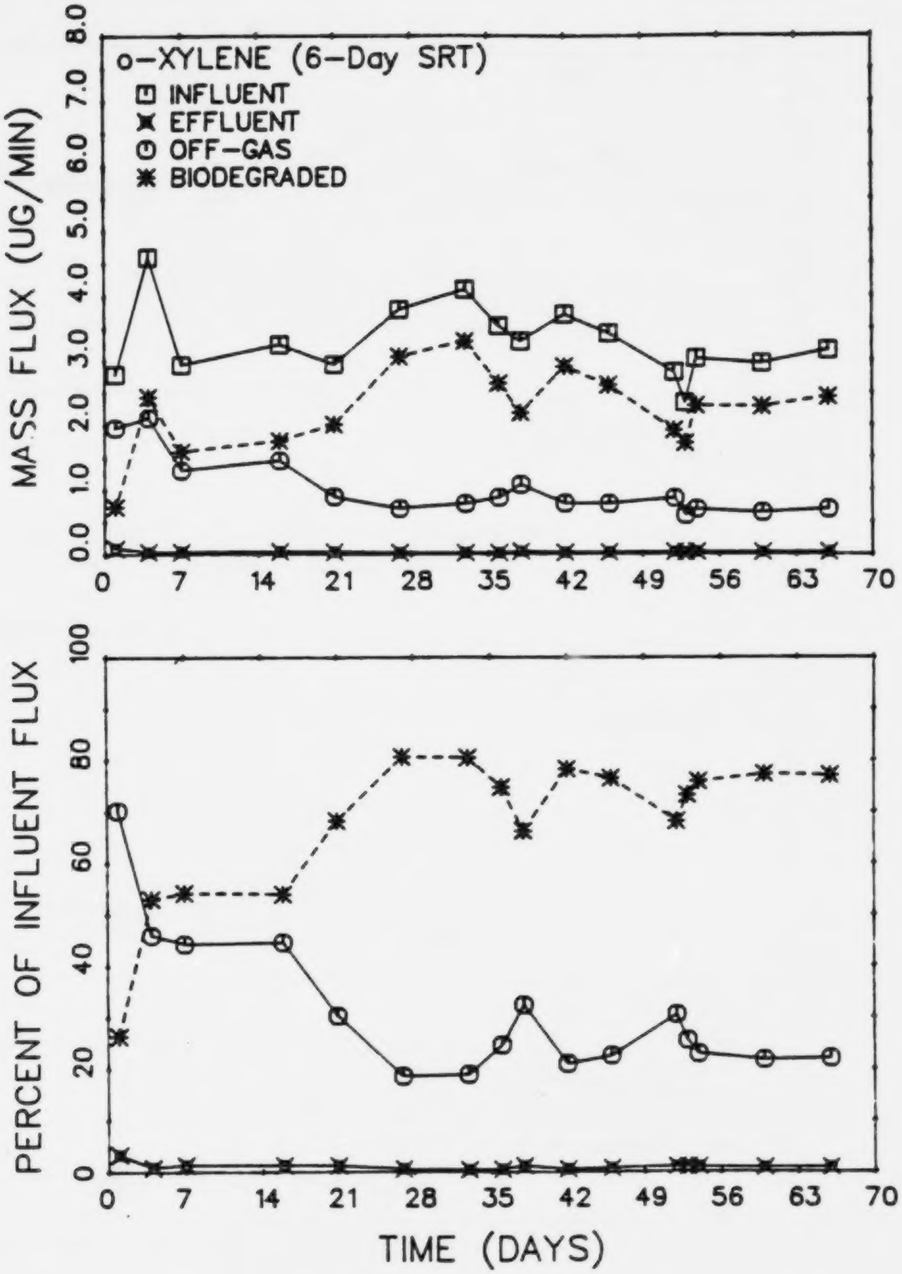


FIGURE 10-56. o-Xylene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 6-day SRT activated sludge study, XYL-AS2.

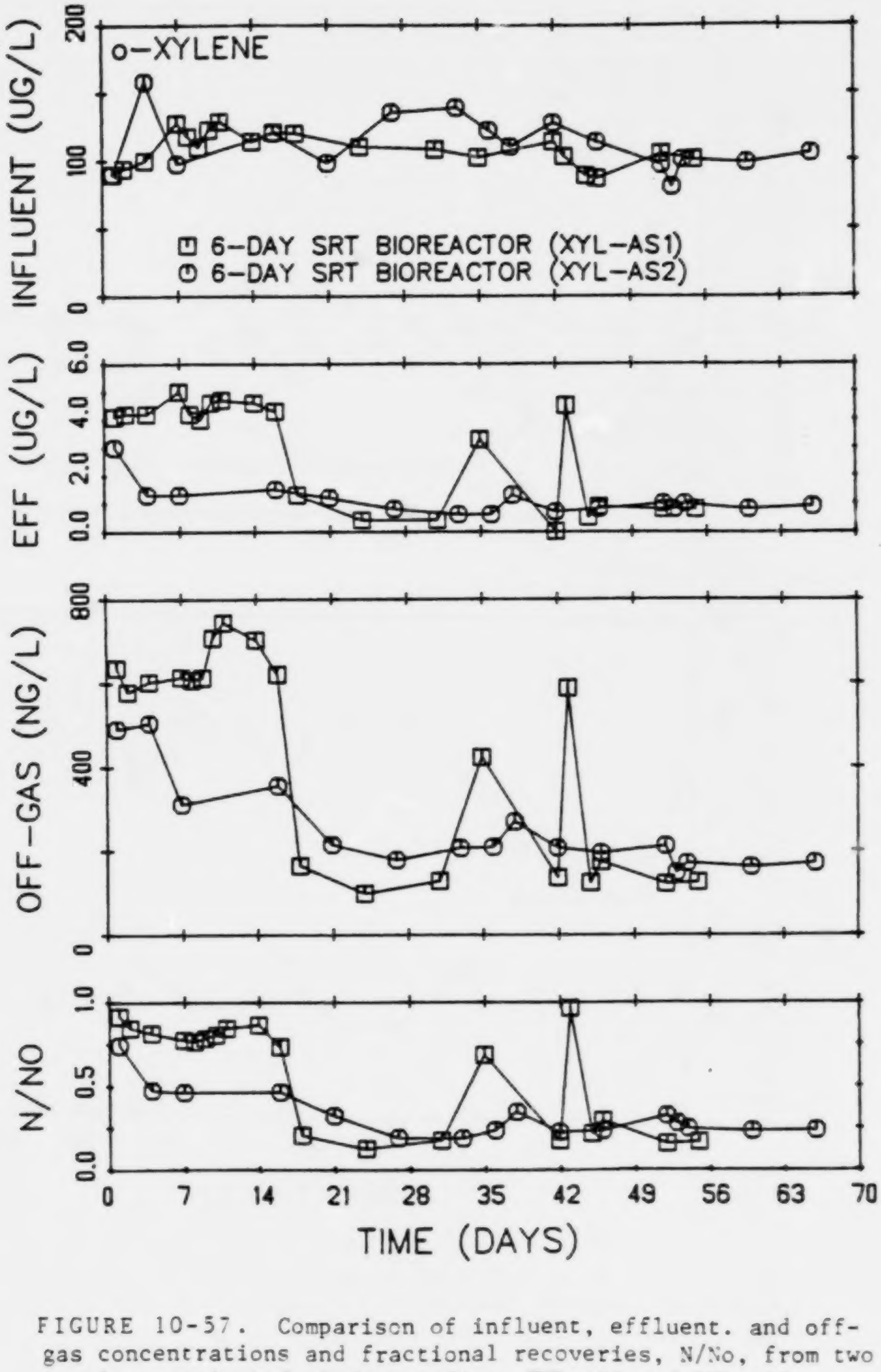


FIGURE 10-57. Comparison of influent, effluent. and off-gas concentrations and fractional recoveries, N/No, from two o-xylene activated sludge studies, XYL-AS1 and XYL-AS2, conducted with 6-day solids retention times.

removals of 80% and 76% for reactors XYL-AS1 and XYL-AS2, respectively. Figures 10-54 and 10-56 compare mass fluxes of o-xylene out of the reactor in effluents and off-gases to the amount removed by biodegradation. The amount biodegraded was calculated from the CMF reactor mass balance equation for o-xylene. In both studies the initial sample on Day 1 indicated that more than 70% of the o-xylene was stripped to the atmosphere, less than 25% was removed by biodegradation and less than 5% was measured in the effluent. The primary effect of microbial biodegradation on the distribution of o-xylene was a significant reduction in the amount stripped to the atmosphere. After the acclimation phase over 70% of o-xylene was degraded, less than 25% was measured in the off-gas, and less than 2% was found in the effluent.

Bioreactor performances with respect to o-xylene removal during the acclimation periods were different in the two 6-day SRT units. The acclimation period in Reactor XYL-AS2 was characterized by significantly lower effluent and off-gas concentrations compared with Reactor XYL-AS1. After an initial drop from 0.74 on Day 1 to 0.47 on Day 4, the N/N_0 values recorded for Reactor XYL-AS2 remained relatively constant for two weeks, and then decreased to approximate steady-state conditions. The acclimation period in Reactor XYL-AS1 resembled the acclimation period observed for ethylbenzene in Reactor EB-AS1. The N/N_0 values averaged approximately 0.80 until Day 16 and then rapidly decreased to 0.20 in two days.

Both 6-day SRT activated sludge units were operated under approximate steady-state conditions for at least five weeks. Effluent and off-gas concentrations remained relatively constant in Reactor XYL-AS2 after the acclimation period and averaged 0.9 μg/ℓ and 192 ng/ℓ, respectively, compared to values of 4.8 μg/ℓ and 731 ng/ℓ that were predicted to occur in the absence of o-xylene biodegradation. The results for Reactor X-AS1 presented in Figure 10-53 show two periods when the removal of o-xylene deviated from steady-state effluent and off-gas concentrations of 0.7 μg/ℓ and 141 ng/ℓ, respectively. On both occasions the effluent and off-gas concentrations significantly increased resulting in N/N_0 values of 0.68 on Day 35 and 0.96 on Day 43. The 96% o-xylene recovery on Day 43 indicated essentially no biodegradation of o-xylene occurred and all of the o-xylene entering the bioreactor was recovered in the effluent and off-gas combined. After both upsets the reactor returned to steady-state levels within several days. No variations in TOC removal or MLSS concentrations occurred during the period of reduced o-xylene biodegradation. A sudden, temporary (less than twelve hours) drop in pH from 7.2 to between 6.0 and 6.2 coincided with both upset periods with respect to o-xylene biodegration. The reduced pH of the mixed liquor had an inhibitory effect on the microorganisms responsible for o-xylene degradation.

The results from an activated sludge bioreactor operated with a 12-day solids retention time presented in Figures 10-58 and 10-59 were characterized by three distinct operating periods with respect to o-xylene removal: an acclimation period, steady-state removal period, and an upset period followed by a return to near steady-state levels. Following the three to four week long acclimation phase was a period of relatively steady-state removal of o-xylene which occurred between Days 29 and 63. The mean steady-state overall o-xylene removal due to biodegradation was 75%. Effluent and off-gas concentrations and N/N_0 values observed during the 12-day SRT study were similar to those measured in the 6-day SRT activated sludge units as shown by the comparisons in Figure 10-60. During the steady-state o-xylene degradation phase, the effluent and off-gas concentrations averaged 1.1 μg/ℓ and 190 ng/ℓ, respectively, while the mean influent concentration was 100 μg/ℓ for the 12-day SRT study.

An upset period during the 12-day SRT study occurred on Day 65 when the recovery of o-xylene suddenly increased to approximately 95% indicating a significant reduction in the amount of o-xylene being biodegraded. Poor o-xylene biodegradation was observed during the next seven days as N/N_0 values averaged 0.68. The overall removal of o-xylene increased to approximately 70% on Day 75 and remained at that level for the next 2 days after which time the study was ended. As observed in previous activated sludge studies, the sudden decrease in o-xylene biodegradation coincided with a temporary reduction in mixed liquor pH to approximately 6.0. Unlike the results from studies with benzene and ethylbenzene, o-xylene biodegradation in the 12-day SRT bioreactor did not immediately return to previous steady-state levels. While the exact length of time the pH was reduced is unknown, the reduction appears to have been of sufficient duration to have a pronounced impact upon the organisms responsible for o-xylene biodegradation. The reactor response between Days 65 and 75 represented a reacclimation period of the activated sludge to o-xylene. The study was not continued long enough to determine whether or not the amount of o-xylene removed by biodegradation would return to the level observed between Days 29 and 63.

Compilations of influent, effluent, and off-gas concentrations averaged during steady-state periods of o-xylene biodegradation are given in Table 10-19 for the three activated sludge studies. Table 10-19 also lists mean effluent and off-gas concentration predicted to occur by the air stripping model if only volatilization effected the distribution of o-xylene between the aqueous and gaseous phases. The steady-state overall removal, or amount biodegraded, was approximately the same in all of the o-xylene activated sludge bioreactors as shown by the comparisons in Figure 10-61. While steady-state removals were similar, significant differences existed among the removals observed during acclimation phases. The effect of biodegradation on the fate of o-xylene during activated sludge treatment in the 10-liter bioreactors is summarized by Table 10-20.

The air-stripping model previously developed was used to predict off-gas concentrations and N/N_0 values from the measured effluent concentrations. Comparisons of measured data points and predicted values represented by dashed lines are shown in Figures 10-62, 10-63 and

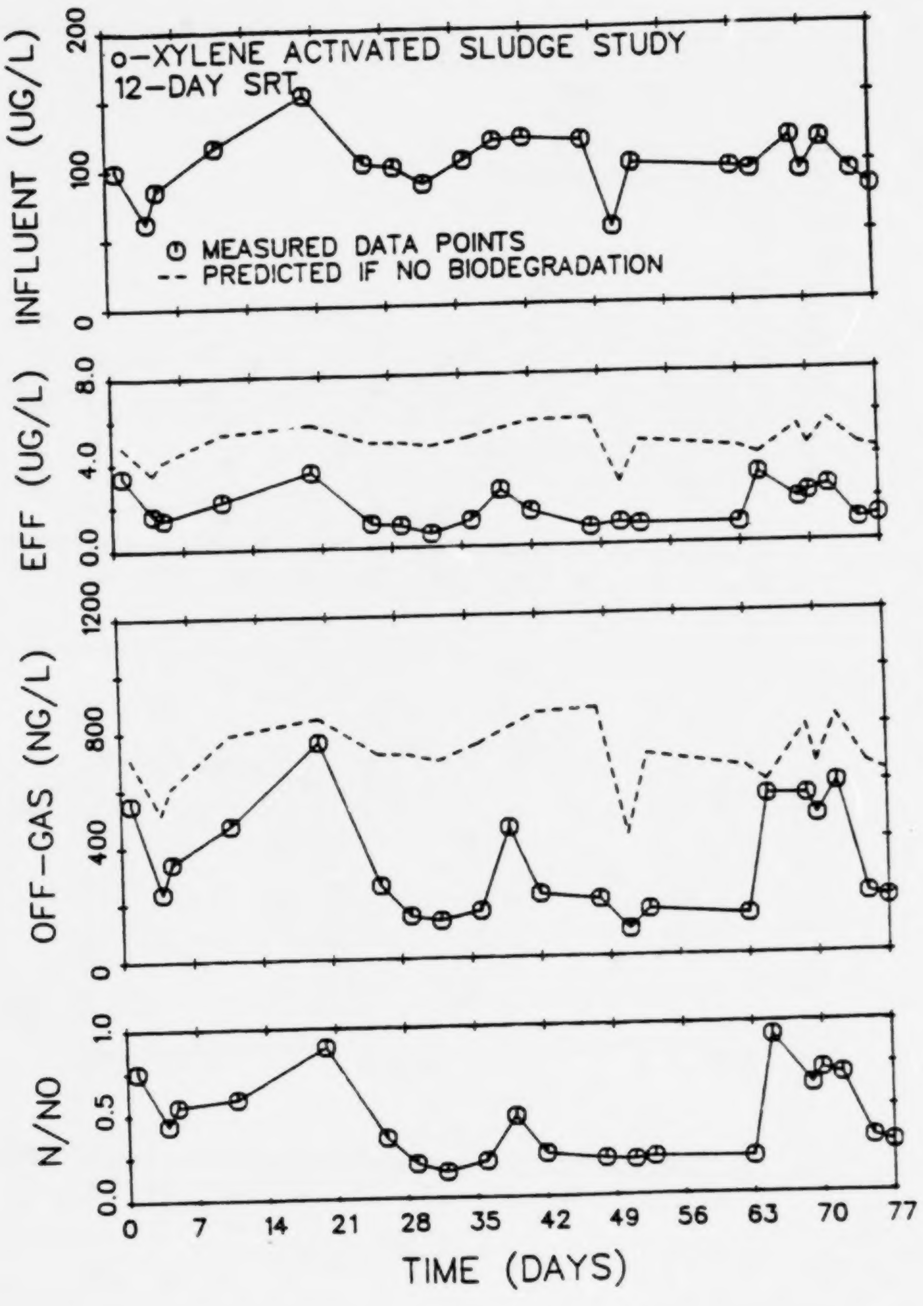


FIGURE 10-58. o-Xylene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during a 12-day SRT o-xylene activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

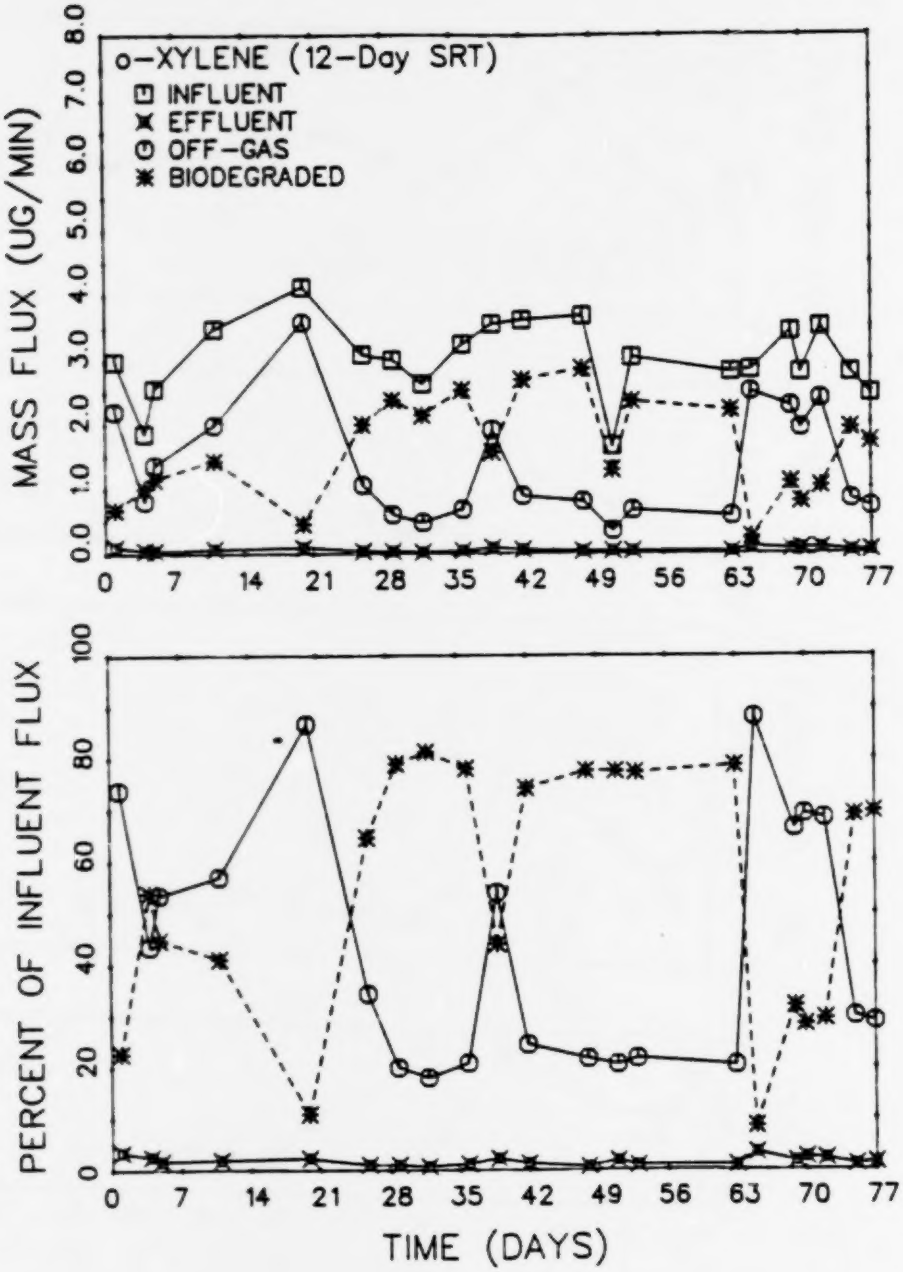


FIGURE 10-59. o-Xylene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the 12-day SRT activated sludge study.

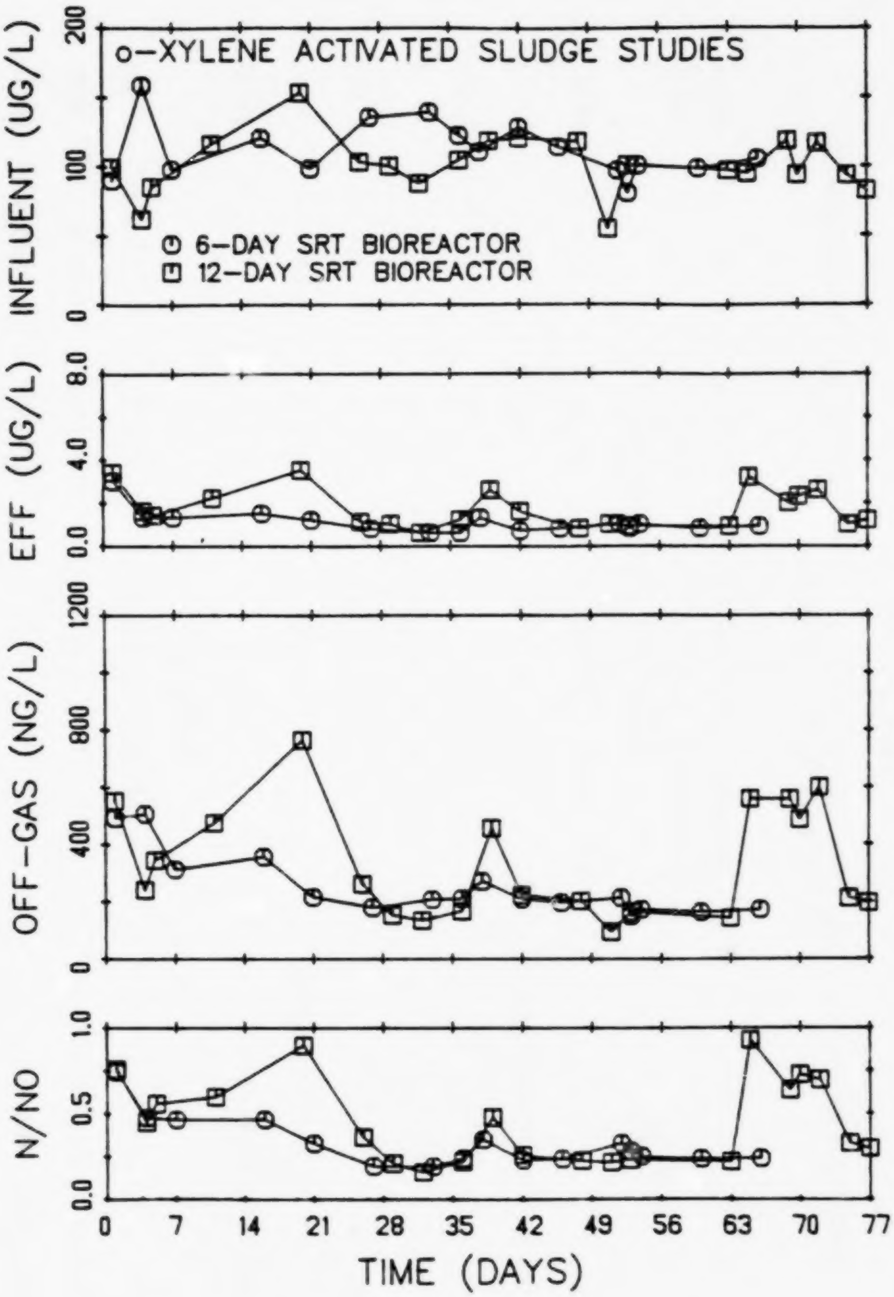


FIGURE 10-60. Comparison of influent, effluent, and off-gas concentrations and fractional recoveries, N/No, from o-xylene activated sludge studies conducted with 6 (XYL-AS2) and 12-day solids retention times.

TABLE 10-19

COMPARISON OF MEASURED AND PREDICTED EFFLUENT AND OFF-GAS O-XYLENE CONCENTRATIONS FROM ACTIVATED SLUDGE BIOREACTORS

	Influent (µg/ℓ)	Effluent (µg/ℓ)	Off-Gas (ng/ℓ)	N/N_o (-)	Removal (%)
		6-DAY SRT; REACTOR XYL-AS1			
Measured	103.(10.2)	0.7(0.3)	141(21)	0.20(0.04)	80(4)
Predicted if no biodegradation	--	4.8(0.7)	731(54)	1.00(0.0)	0(0)
Predicted form effluent	--	--	107(38)	0.15(0.06)	85(6)
		6-DAY SRT; REACTOR XYL-AS2			
Measured	111.9	0.9(0.2)	192(33)	0.24(0.05)	76(5)
Predicted if no biodegradation	--	5.3(0.9)	782(135)	1.00(0.0)	0(0)
Predicted from effluent	--	--	125(30)	0.17(0.05)	83(5)
		12-DAY SRT			
Measured	100.2(17.1)	1.1(0.4)	190(59)	0.25(0.06)	75(6)
Predicted if no biodegradation	--	4.9(0.8)	720(121)	1.00(0.0)	0(0)
Predicted from effluent	--	--	167(52)	0.24(0.07)	76(7)

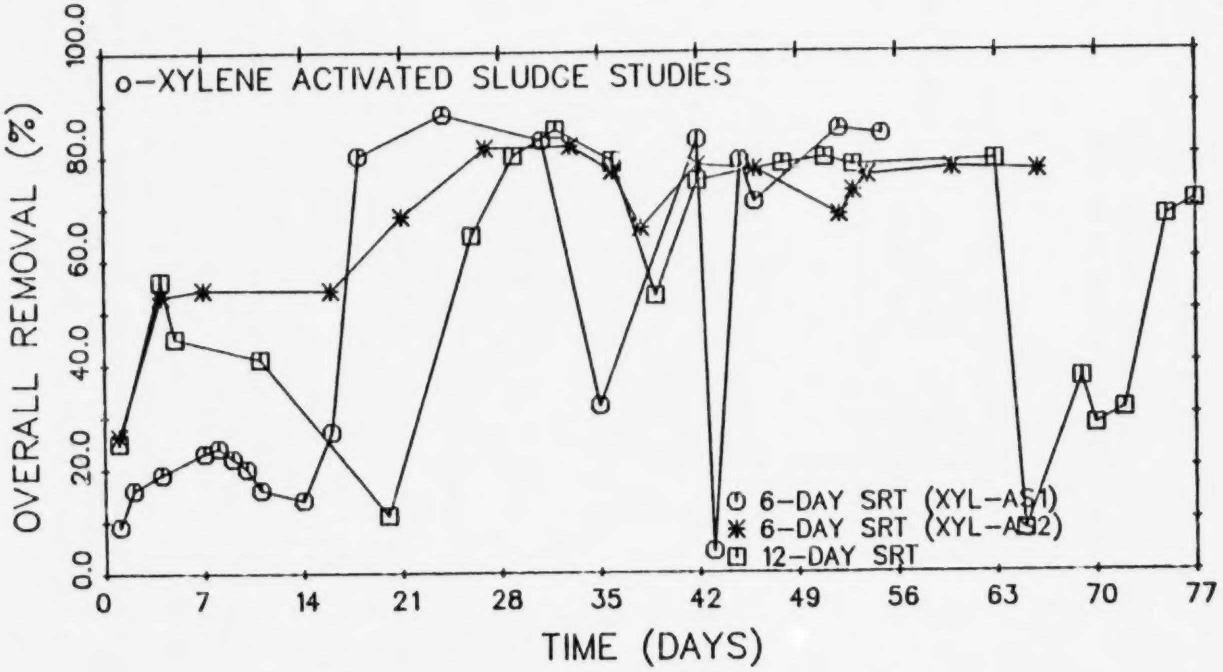


FIGURE 10-61. Overall o-xylene removals due to biodegradation measured during activated sludge studies conducted in 10-liter bioreactors operated with 6 and 12-day solids retention times.

10-64 for the three activated sludge studies. In general, the model predicted values were in reasonable agreement with the measured values.

TABLE 10-20

FATE OF O-XYLENE DURING STEADY-STATE BIODEGRADATION BY ACTIVATED SLUDGE

	Percent of Influent Flux		
	6-Day SRT (XYL-AS1)	6-Day SRT (XYL-AS2)	12-Day SRT
Effluent	1	1	1
Off-Gas	19	23	24
Biodegraded	80	76	75
Biosorbed	0	0	0
Days	18-31,44-55	27-66	29-63

10.4.2.5. Chlorobenzene

Activated sludge bioreactor studies with chlorobenzene were conducted at solids retention times of 6 and 12 days. Results from the 6-day SRT study are presented in Figures 10-65 and 10-66, while results from the 12-day study are given by Figures 10-67 and 10-68, respectively. Figures 10-65 and 10-67 depict influent, effluent and off-gas concentrations and N/N_0 values measured during the activated sludge studies. Dashed lines represent effluent and off-gas concentrations predicted to occur if only air-stripping effected a reduction in the aqueous concentration. Figures 10-66 and 10-68 show mass flux values obtained by combining measured concentrations with appropriate aqueous and off-gas flow rates. The amount biodegraded, represented by a dashed line, was calculated from a mass balance equation for chlorobenzene.

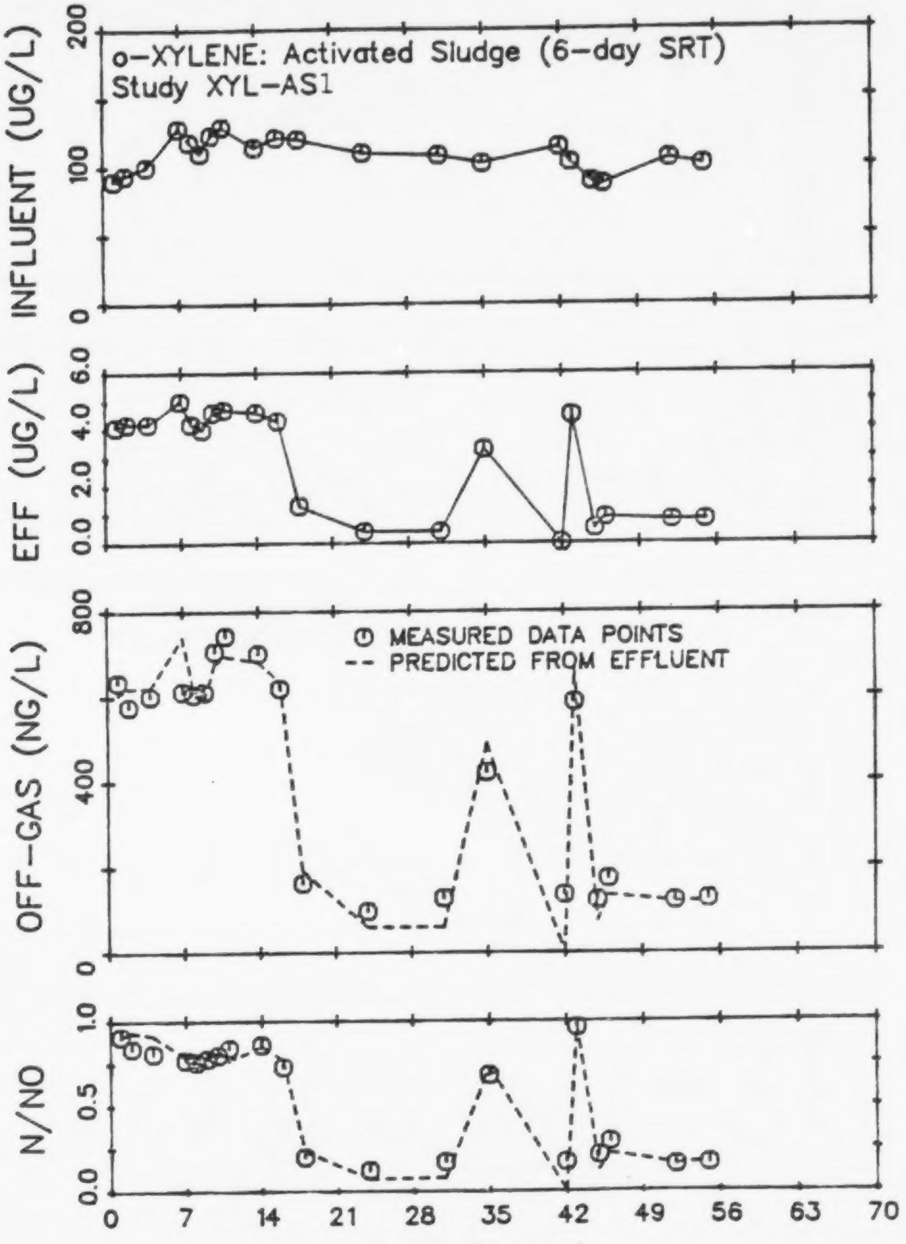


FIGURE 10-62. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 6-day SRT activated sludge study with o-xylene, XYL-AS1.

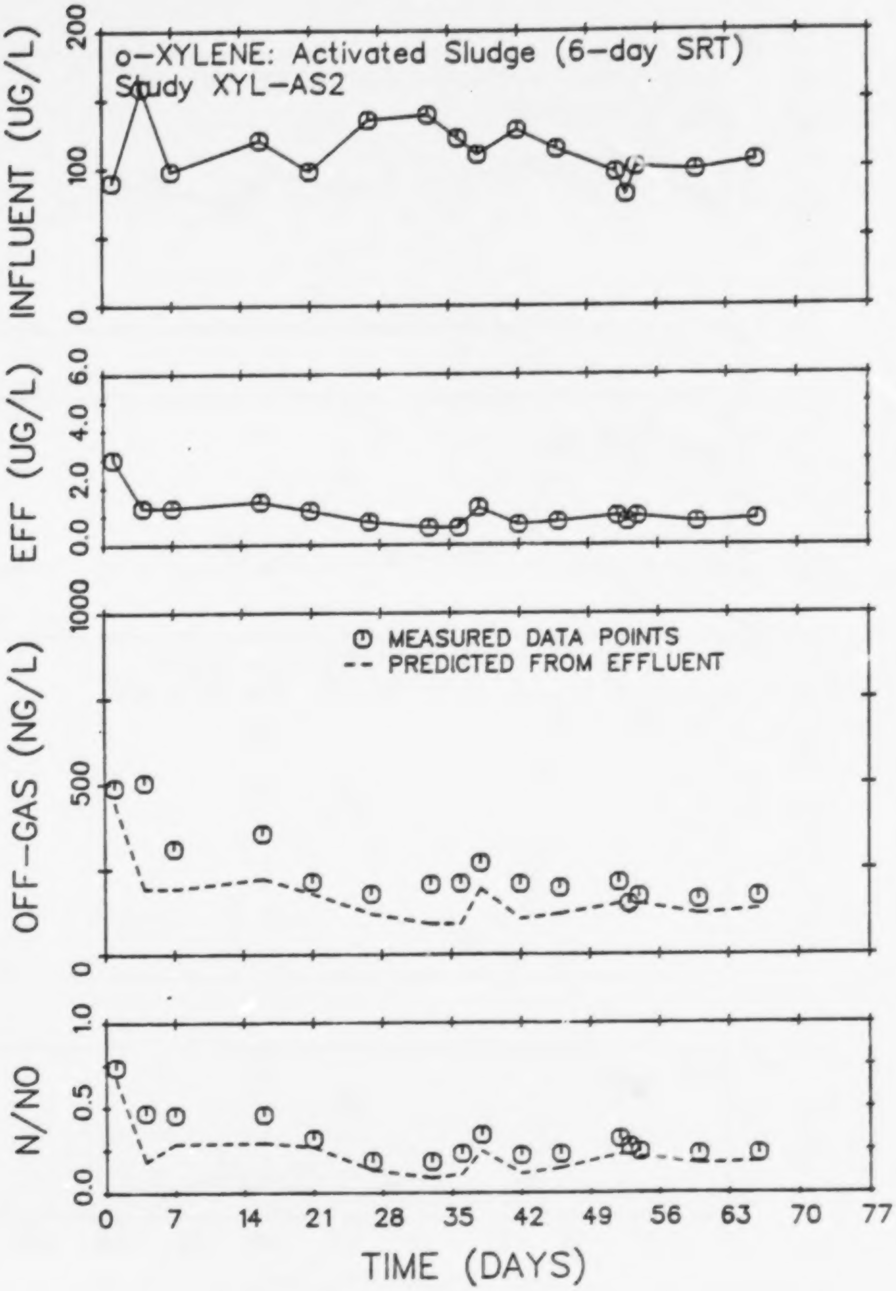


FIGURE 10-63. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 6-day SRT activated sludge study with o-xylene, XYL-AS2.

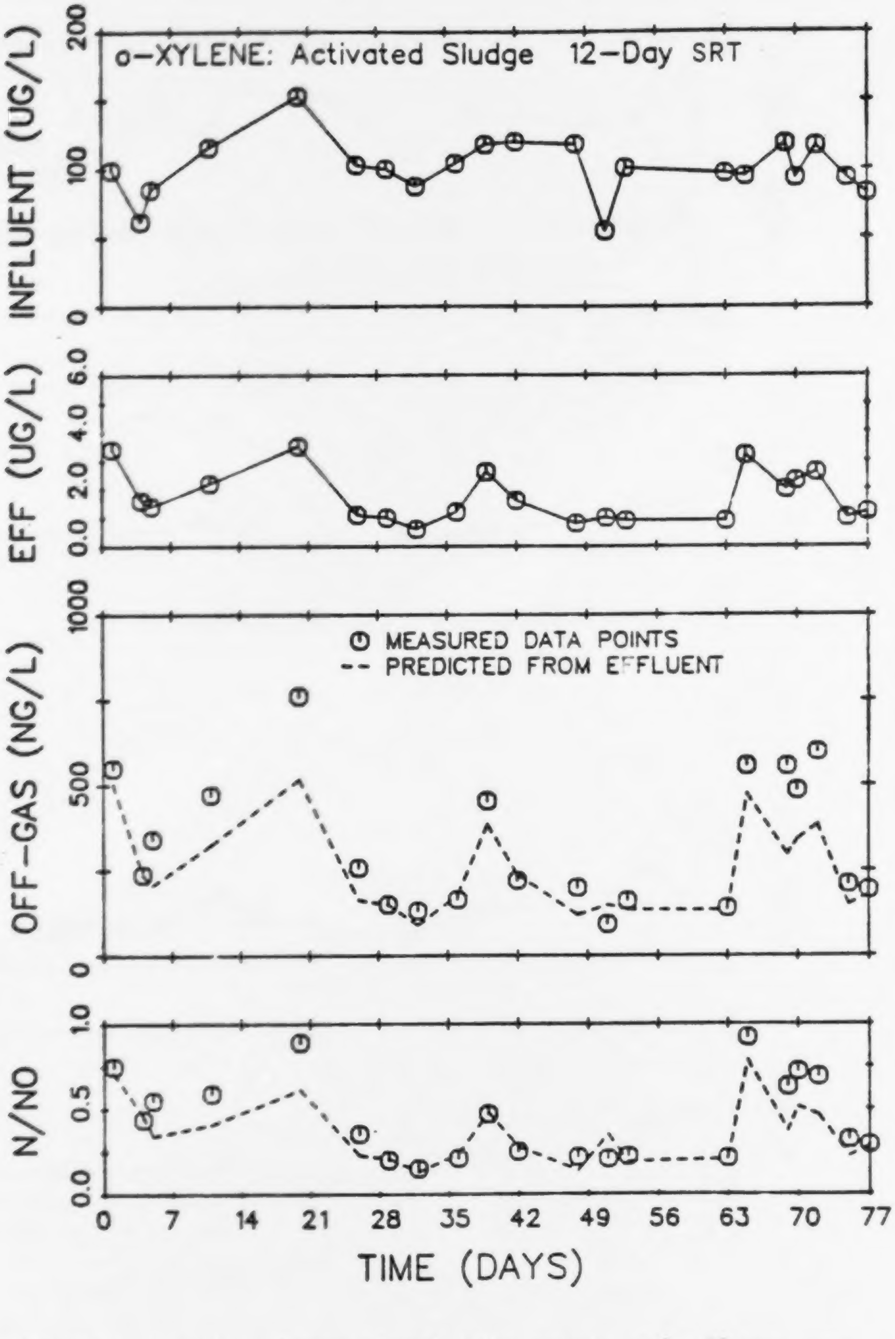


FIGURE 10-64. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations for the 12-day SRT activated sludge study with o-xylene.

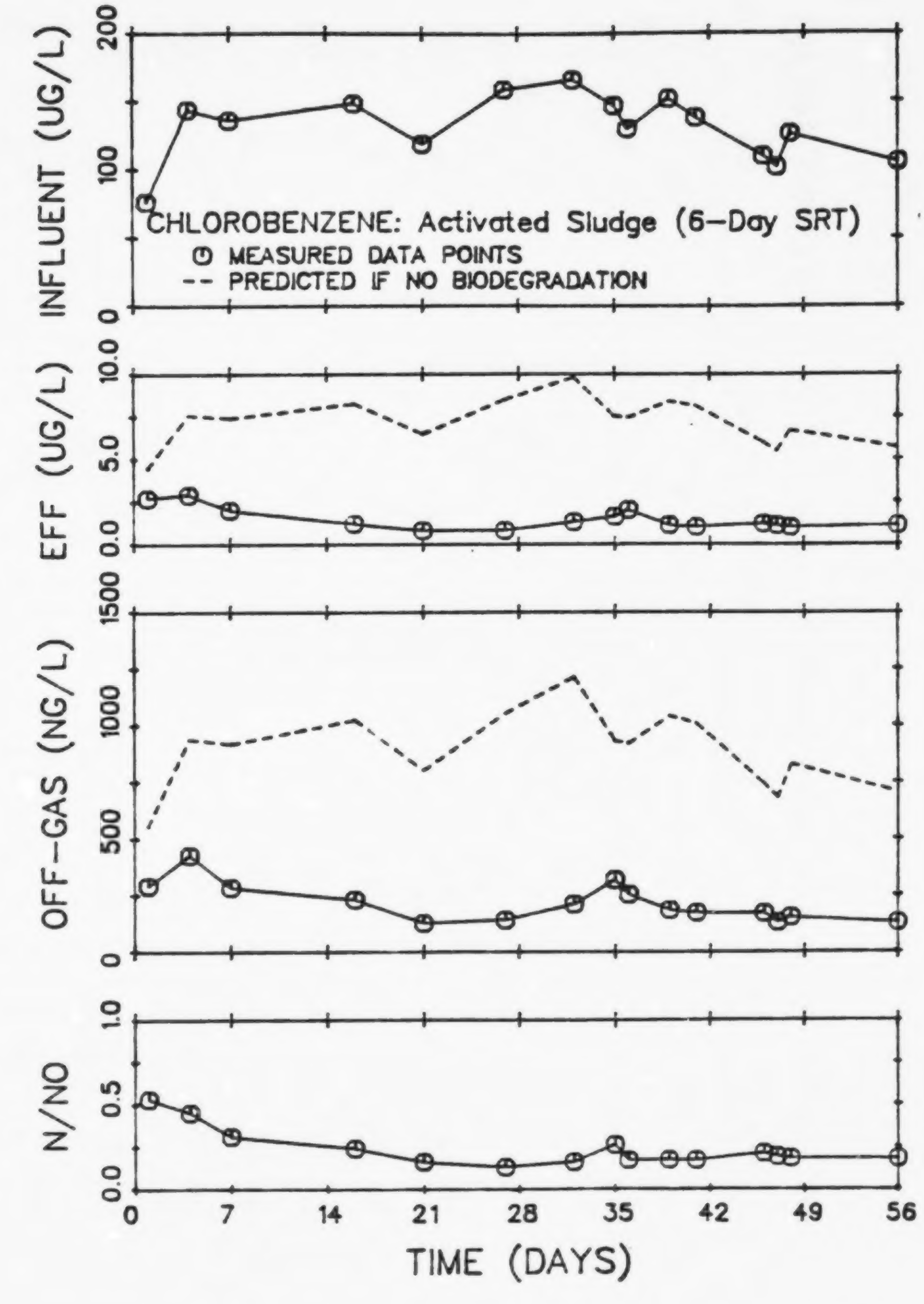


FIGURE 10-65. Chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the chlorobenzene 6-day SRT activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

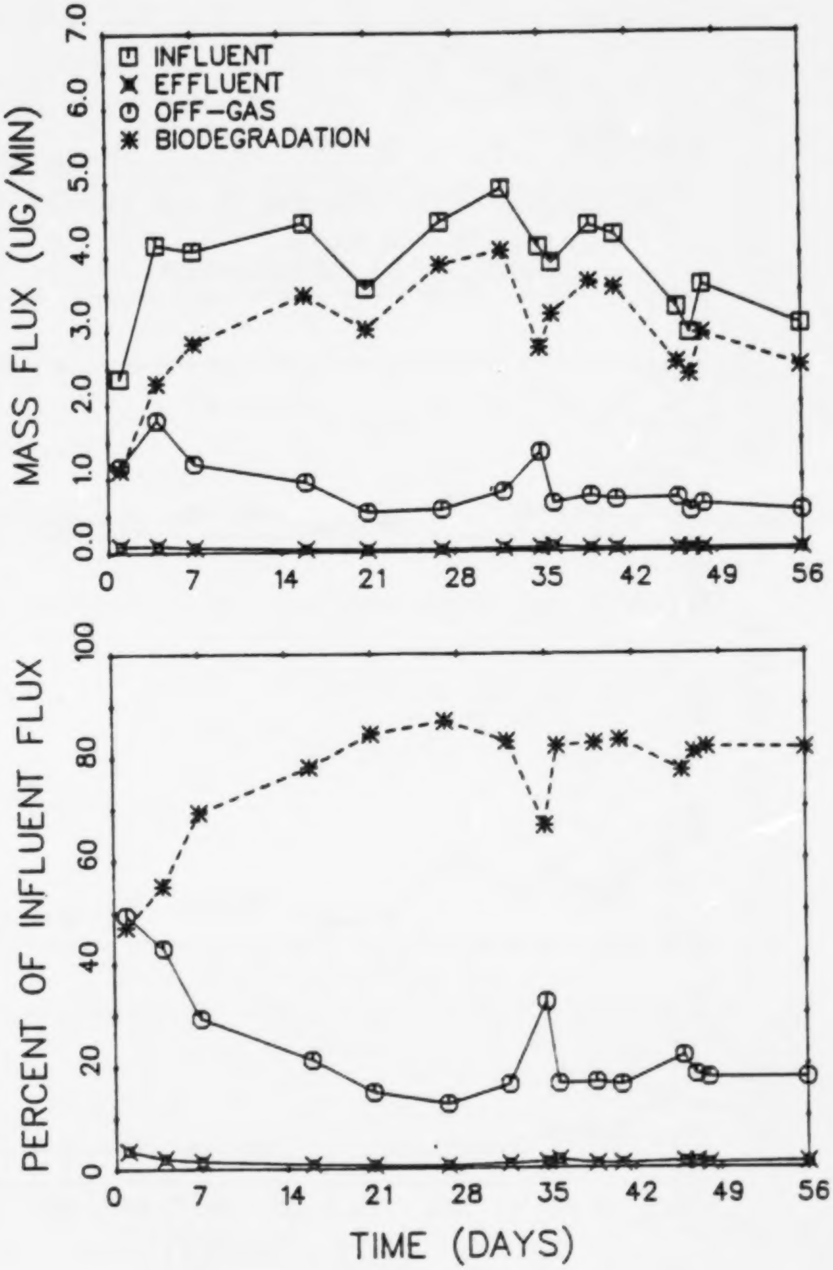


FIGURE 10-66. Chlorobenzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the chlorobenzene 6-day SRT activated sludge study.

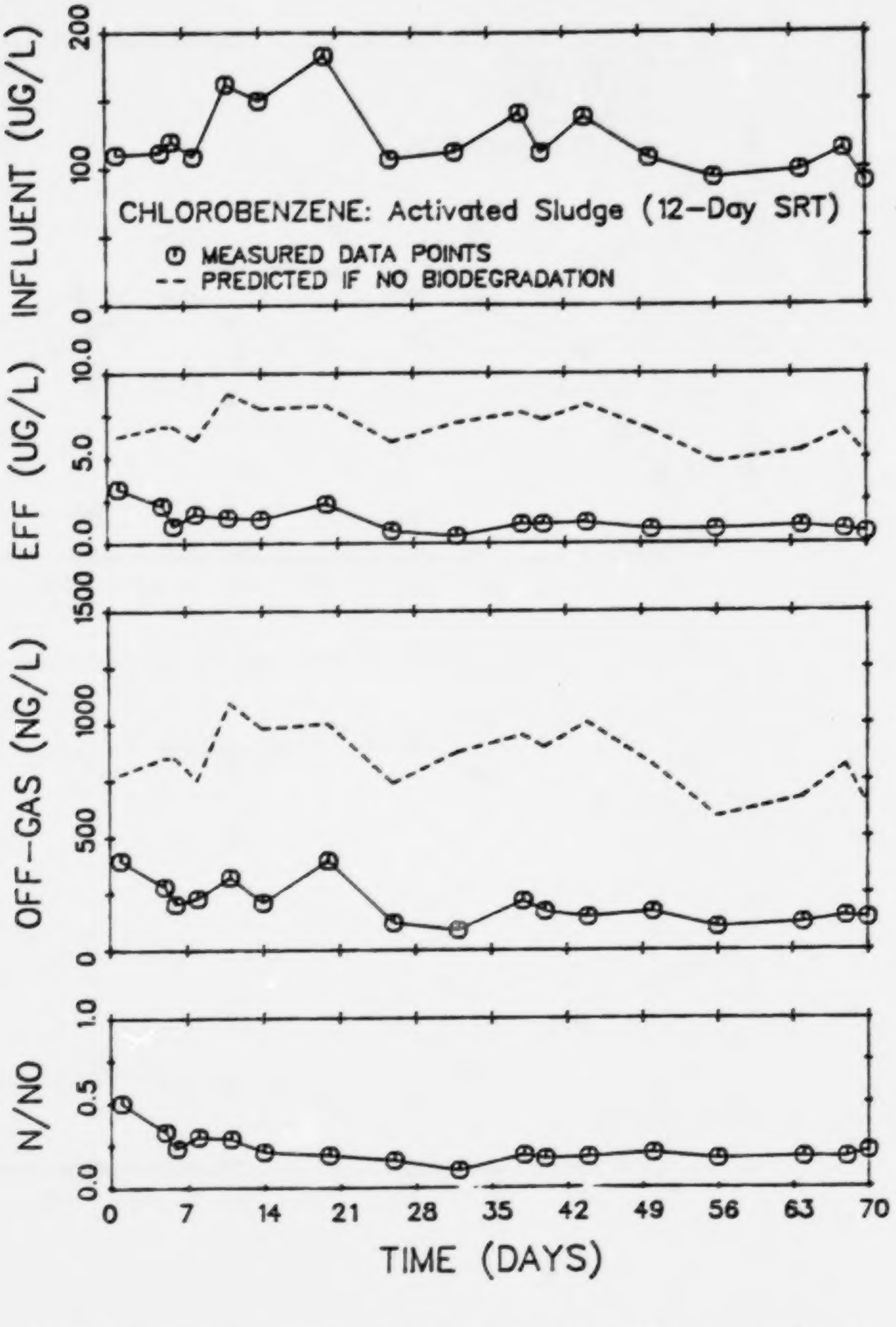


FIGURE 10-67. Chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the chlorobenzene 12-day SRT activated sludge study. (Dashed lines give values predicted to occur in the absence of biodegradation.)

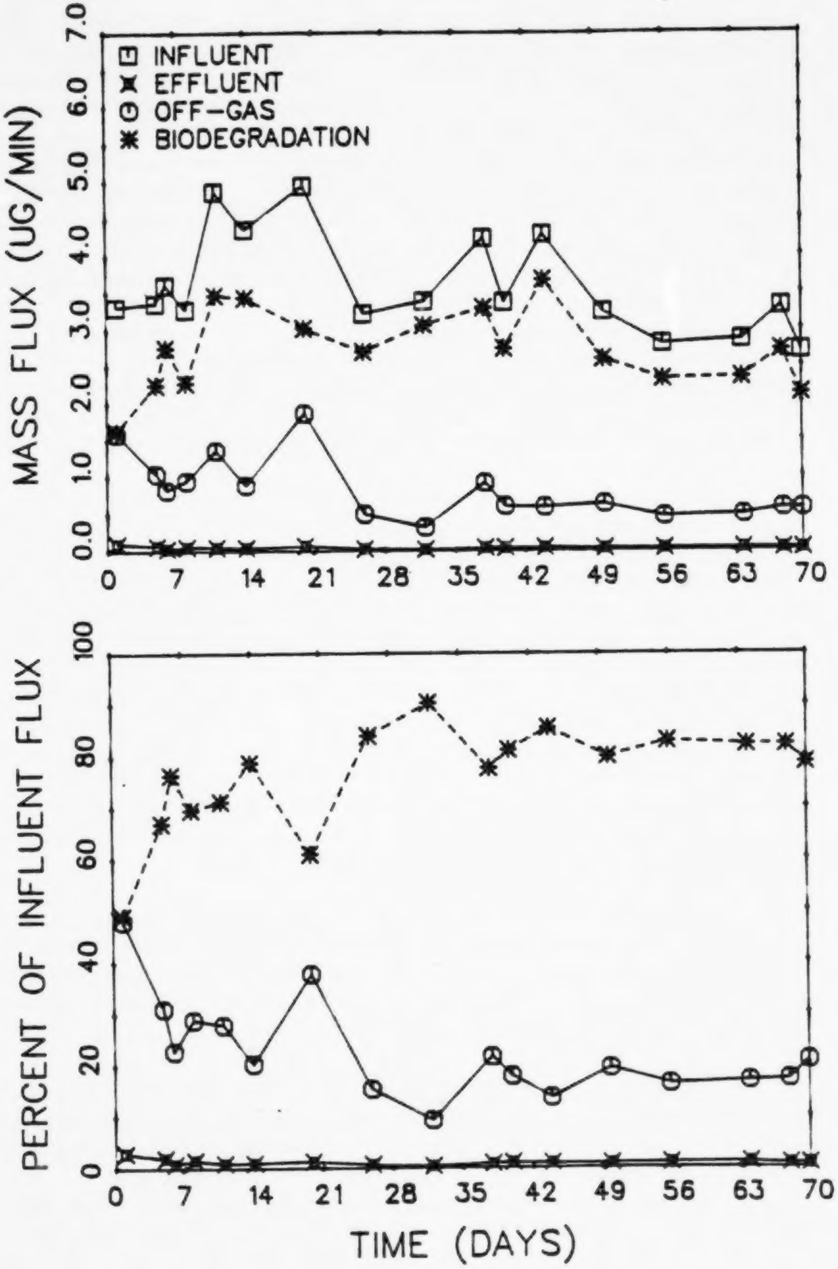


FIGURE 10-68. Chlorobenzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the chlorobenzene 12-day SRT activated sludge study.

Biodegradation of chlorobenzene was observed in both of the activated sludge studies and was evidenced by measured mass fluxes out of the bioreactors (effluent and off-gas fluxes combined) which were significantly less than the measured influent fluxes. This disappearance of chlorobenzene averaged greater than 80% during steady-state operating periods. The effect of biodegradation is illustrated by the differences between measured effluent and off-gas data points and the dashed lines in Figures 10-65 and 10-67. While recoveries of chlorobenzene in baseline studies without activated sludge averaged approximately 95%, the maximum recoveries in the activated sludge studies of 50 to 55% on Day 1 indicated there was an immediate, partial acclimation of the activated sludge microorganisms to chlorobenzene. The acclimation period lasted between two and three weeks during which time the amount of chlorobenzene biodegraded increased from 50% on Day 1 to steady-state levels of greater than 80%. Effluent and off-gas concentrations were both reduced by similar amounts which averaged approximately 80%. Since the off-gas flux represented nearly 95% of the total flux out of the reactor, the primary effect of biodegradation was a reduction in the amount of chlorobenzene stripped to the atmosphere.

The two activated sludge studies were continued for at least five weeks after the initial acclimation periods. Average effluent and off-gas concentrations during the steady-state period in the 6-day SRT study were 1.1 μg/ℓ and 184 ng/ℓ, respectively, compared to values of 7.4 μg/ℓ and 911 ng/ℓ which would have occurred if chlorobenzene had not been degraded by the activated sludge microorganisms. Similar results were recorded during the 12-day SRT study; effluent and off-gas concentrations averaged 1.0 μg/ℓ and 169 ng/ℓ, respectively, compared to values of 6.7 and 832 predicted to occur in the absence of chlorobenzene biodegradation. The comparison of results from the two studies in Figure 10-69 shows there was no significant difference in the fate of chlorobenzene in activated sludge maintained at 6 and 12-day solids retention times. Summaries of average influent, effluent and off-gas concentrations are tabulated in Table 10-21.

Effluent and off-gas fluxes averaged from the two studies accounted for approximately 0.8 and 17.8%, respectively, of the influent mass flux; the remaining 81.4% was removed by biodegradation by the activated sludge. Table 10-22 summarizes the steady-state mass flux data depicted in Figures 10-66 and 10-68.

Chlorobenzene volatilization in the 10-liter bioreactors was sufficiently characterized to enable off-gas concentrations and N/N_0 values to be accurately predicted from measured effluent concentrations. As shown by the comparisons in Figures 10-70 and 10-71, values predicted by the air-stripping model agreed well with the measured data. As an illustration, the predicted off-gas concentration for the 6-day SRT study was 147 ug/l and the measured value was 184 ug/l. The model predicted an overall chlorobenzene removal for that study of 84% while the measured value was 82%. Similar agreement between predicted and measured values occurred for the 12-day SRT study.

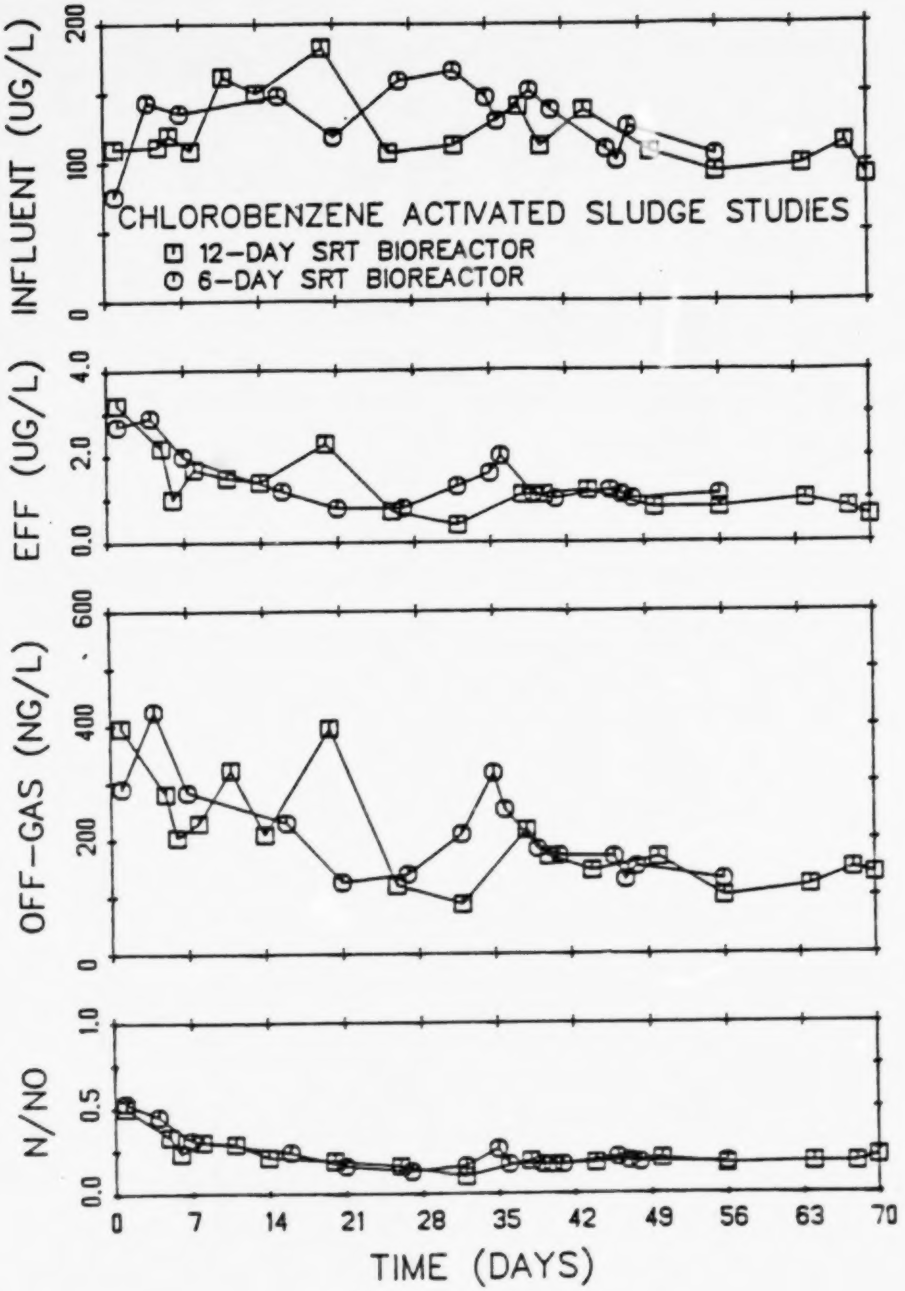


FIGURE 10-69. Comparison of influent, effluent, and off-gas concentrations and fractional recoveries, N/No, from chlorobenzene activated sludge studies conducted with 6 and 12-day solids retention times.

TABLE 10-21

SUMMARY OF STEADY-STATE AVERAGE CHLOROBENZENE CONCENTRATIONS FROM ACTIVATED SLUDGE BIOREACTOR STUDIES CONDUCTED WITH 6 AND 12-DAY SRT'S

	Influent (ug/l)	Effluent (ug/l)	Off-Gas (ug/l)	N/N_o (-)	Removal (%)
6-DAY SRT					
Measured	133.4 (21.6)$^+$	1.1 (0.3)	184 (57)	0.18 (0.03)	82 (2.9)
Predicted if no biodegradation	---	7.4 (1.3)	911 (164)	1.00 (0.0)	0.0 (0.0)
Predicted from effluent	---	---	147 (42)	0.16 (0.05)	84 (5.1)
12-DAY SRT					
Measured	120.4 (27.3)	1.0 (0.5)	169 (82)	0.18 (0.03)	82 (3.0)
Predicted if no biodegradation	---	6.7 (1.2)	832 (146)	1.00 (0.0)	0.0 (0.0)
Predicted from effluent	---	---	126 (60)	0.15 (0.05)	85 (5.0)

+ Numbers in parentheses are standard deviations

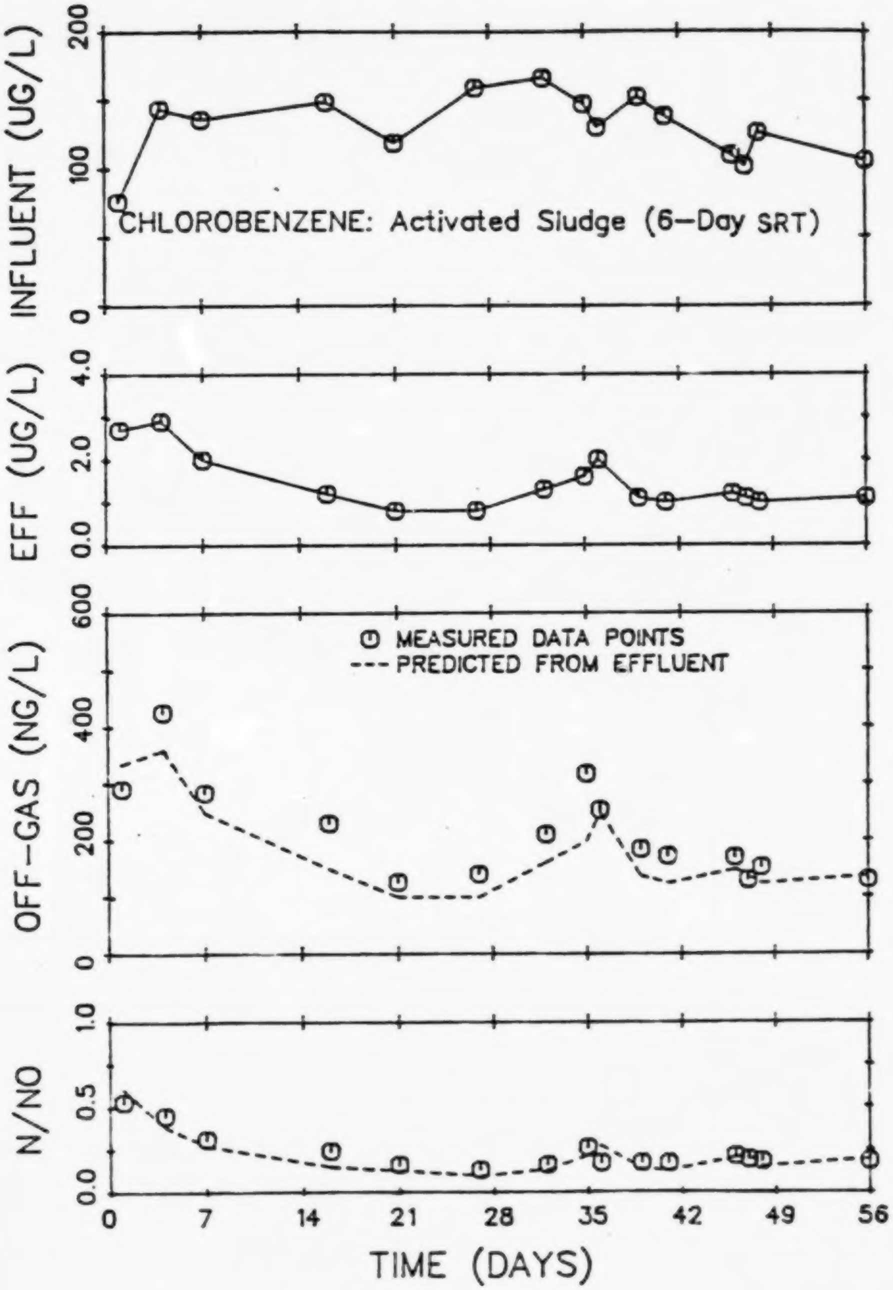


FIGURE 10-70. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations from the 6-day SRT activated sludge study with chlorobenzene.

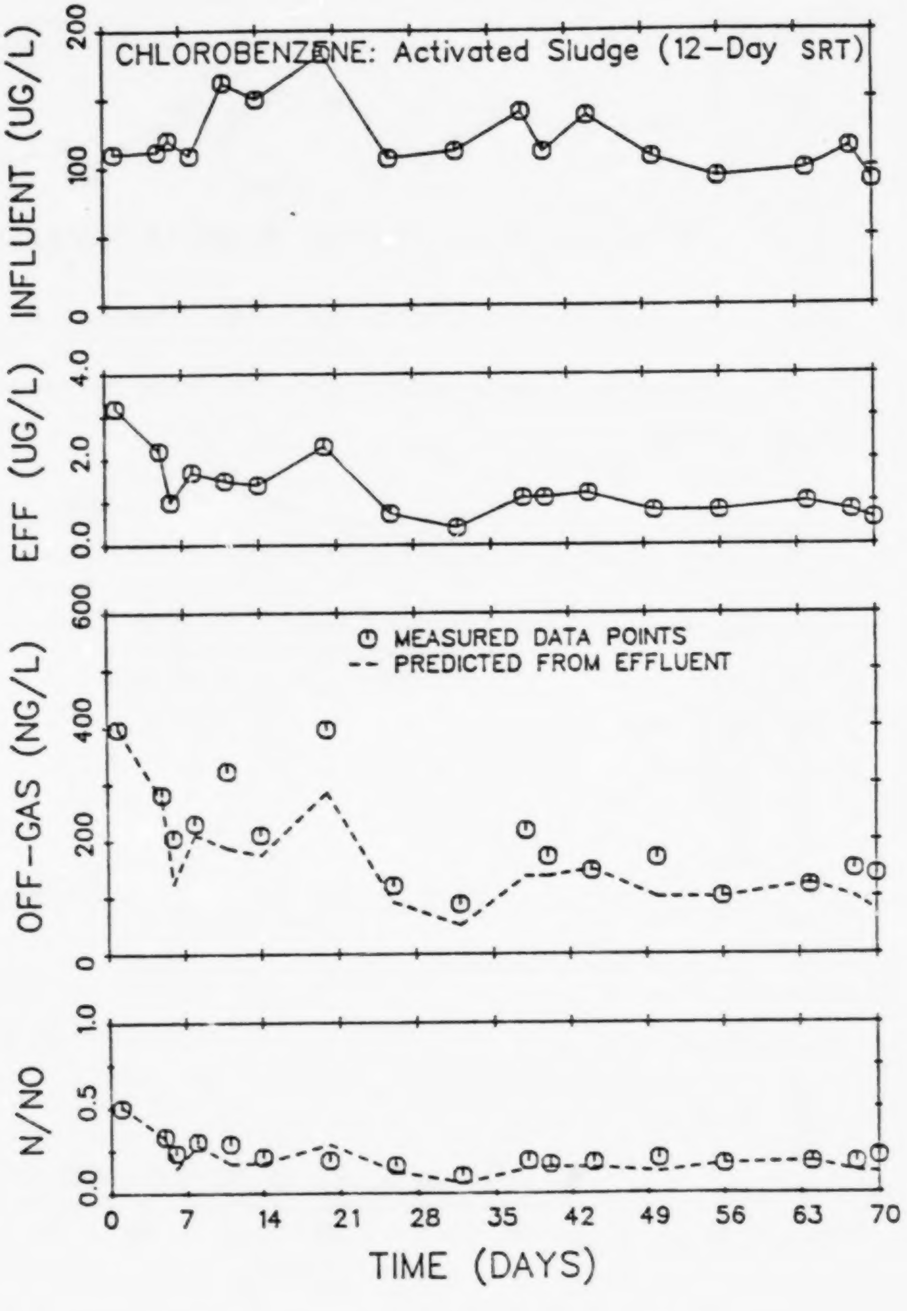


FIGURE 10-71. Experimental data points and off-gas concentrations and fractional recoveries, N/No, predicted from measured effluent concentrations from the 12-day SRT activated sludge study with chlorobenzene.

TABLE 10-22

FATE OF CHLOROBENZENE DURING STEADY-STATE BIODEGRADATION BY ACTIVATED SLUDGE

	Percent of Influent Flux	
	6-Day SRT	12-Day SRT
Effluent	0.8	0.8
Off-Gas	18.5	17.2
Biodegraded	80.7	82.0
Biosorbed	0	0
Days	21-56	26-70

10.5 DETERMINATION OF BIODEGRADATION RATE COEFFICIENTS

Two methods were used to quantify the biodegradation rate coefficients for the biodegradable compounds. The first procedure incorporated data from the continuous flow bioreactor studies into a CMF reactor mass balance equation which included volatilization and biodegradation terms. The second approach involved directly measuring the removal of the toxic compounds in batch rate studies with acclimated activated sludges.

10.5.1. CMF Bioreactor Mass Balance Approach

The mass balance equation for a biodegradable compound in a CMF reactor under conditions of steady-state can be written as

$$Q_iC_i = Q_eC_e + Q_gC_g + VC_ek_b + Q_sC_eK_pM_s \qquad (10\text{-}4)$$

mass entering reactor	=	mass leaving in effluent	+	mass leaving in off-gas	+	mass removed due to biodegradation	+	mass sorbed on solids removed in waste sludge

Background equilibrium studies showed that sorption of the biodegradable compounds by the activated sludge biomass was not significant for the low concentrations used in the activated sludge bioreactor studies. Eliminating the sorption term, dividing both sides by the influent flux, Q_iC_i, recognizing that $Q_i = Q_e$ and rearranging gives

$$\frac{VC_ek_b}{Q_iC_i} = 1 - \frac{Q_iC_e + Q_gC_g}{Q_iC_i} \qquad (10\text{-}5)$$

The term $(Q_iC_e+Q_gC_g)/Q_iC_i$ is the fractional recovery of a compound which has been represented by N/N_o. Substituting N/N_o in Equation 10-5 yields

$$\frac{VC_ek_b}{Q_iC_i} = 1 - N/N_o \qquad (10\text{-}6)$$

Rearranging and substituting $\bar{t} = V/Q_i$, Equation 10-6 can be written as

$$\bar{t}k_b = \frac{1-N/N_o}{C_e/C_i} \qquad (10\text{-}7)$$

Substituting for C_e/C_i by Equation 9-26 yields

$$\frac{\bar{t}k_b}{1+\bar{t}(k_b+k_v)} = 1 - N/N_o \qquad (10\text{-}8)$$

Solving for k_b

$$k_b = \frac{(1/\bar{t})(1+\bar{t}k_v)}{N/N_o} - (1/\bar{t})(1+\bar{t}k_v) \qquad (10\text{-}9)$$

Biodegradation rate coefficients for each biodegradable compound were calculated by Equation 10-9 for the single solute activated sludge studies and summarized in Table 10-23. The biodegradation and volatilization rate coefficients reported in Table 10-23 represent the averages of rate coefficients calculated each day bioreactor samples were collected during steady-state biodegradation periods. Rate coefficients determined during the two to three week acclimation periods and upset periods of low toxics removals were not included in the calculations.

The results in Table 10-23 show, that for a given compound, there was not significant variation in the calculated biodegradation rate coefficient, k_b, as a function of solids retention time. Such a result was anticipated since there were no significant differences in overall removals from activated sludge studies conducted at different SRT's. Values of k_b for benzene varied between 0.43 and 0.49 min^{-1} for SRT's ranging from 3 to 12 days. The range of biodegradation rate coefficients calculated for the other biodegradable compounds was: toluene, 0.42 to 0.45 min^{-1}; ethylbenzene, 0.37 to 0.43 min^{-1}; o-xylene, 0.20 to 0.28 min^{-1}; chlorobenzene, 0.26 min^{-1}; 1,2-dichlorobenzene, 0.017

TABLE 10-23

FIRST ORDER BIODEGRADATION RATE COEFFICIENTS CALCULATED FROM CMF REACTOR MASS BALANCES

Compound	Solids Retention Time (days)	Biodegradation Rate Coefficient, k_b (min^{-1})	Volatilization Rate Coefficient, k_v (min^{-1})*	Overall Removal (%)
Benzene	3	0.43 (0.07)	0.081 (0.002)	84
	6	0.43 (0.12)	0.075 (0.002)	83
	12	0.49 (0.15)	0.075 (0.004)	86
Toluene	6	0.45 (0.10)	0.078 (0.003)	83
	12	0.42 (0.13)	0.077 (0.005)	83
Ethylbenzene (EB-AS1)	6	0.37 (0.06)	0.091 (0.004)	80
(EB-AS2)	6	0.43 (0.13)	0.087 (0.004)	81
	12	0.43 (0.11)	0.087 (0.004)	82
o-Xylene (XYL-AS1)	6	0.28 (0.07)	0.062 (0.002)	80
(XYL-AS2)	6	0.20 (0.05)	0.060 (0.002)	76
	12	0.21 (0.06)	0.060 (0.003)	75
Chlorobenzene	6	0.26 (0.04)	0.050 (0.002)	82
	12	0.26 (0.07)	0.052 (0.004)	82
Nitrobenzene	6	0.12 (0.02)	<0.001	97
	6	0.09 (0.01)	<0.001	96
1,2-Dichlorobenzene	6	0.017 (0.004)	0.025 (0.001)	36
	12	0.018 (0.007)	0.026 (0.001)	38

* Calculated from Equation 7-2

to 0.018 min^{-1}; and nitrobenzene 0.09 to 0.12 min^{-1}. The following decreasing order of k_b values for the biodegradable compounds was observed:

benzene ≈ toluene ≈ ethylbenzene > o-xylene ≃ chlorobenzene
> nitrobenzene > 1,2-dichlorobenzene

This order was slightly different than the order of overall removals:

nitrobenzene > benzene ≈ toluene > chlorobenzene ≈ ethylbenzene
> o-xylene > 1,2-dichlorobenzene

Biodegradation rate coefficients calculated by Equation 10-9 from N/N_o values (or overall removals) are a function of the volatilization rate coefficient, k_v. For a given N/N_o value the larger the volatilization rate coefficient, the larger the biodegradation rate coefficient must be to accomplish the same level of removal. Assuming the amount of each compound biodegraded during activated sludge treatment averaged 80%, the data in Table 10-24 illustrates that as the compound volatility increases, the rate of biodegradation also increases. The ratio k_b/k_o, where $k_o = k_b + k_v$, is approximately 0.80 for each compound, except 1,2-dichlorobenzene and nitrobenzene, in Table 10-24 indicating that biodegradation accounts for 80% of the reduction in aqueous concentration. This explains why the biodegradation rate coefficient of chlorobenzene was considerably smaller than that of benzene even though the amount of each compound biodegraded was approximately the same. The same explanation applies to the extremely different positioning of nitrobenzene in the relative orders of overall removals and biodegradation rate coefficients. While the amount of nitrobenzene removed by biodegradation was the largest, its biodegradation rate coefficient was the smallest of the six highly biodegradable compounds. Nitrobenzene was only slightly volatile in the experimental system; its volatilization rate coefficient (estimated) was approximately two orders of magnitude less than those of benzene, toluene, and ethylbenzene. Therefore, the biodegradation rate coefficient required to effect overall removals in excess of 95% was approximately one-fourth the value of those calculated for the volatile compounds.

Although all of the activated sludge studies were conducted with aeration rates in the range of 3.5 to 4.5 ℓ/min, the average aeration rate of individual studies varied from study to study. Table 10-25 illustrates the sensitivity of the model used to calculate k_b to variations in the aeration rate coefficient. The examples were calculated for benzene assuming a 5.5 hour mean hydraulic retention time. An increase in aeration rate from 3.5 to 4.5 resulted in an increase in k_b from 0.39 to 0.49 min^{-1} for an overall removal of 85%.

Another operating parameter that entered into the model to calculate k_b was the hydraulic retention time, $\bar{t}$. As Table 10-26 shows, variations in $\bar{t}$, from 4.5 to 6.5 hours, did not have an effect upon the calculated values of k_b. The examples in Table 10-26 were calculated assuming an 85% overall removal of benzene at an aeration rate of 4.0 ℓ/min. The range of mean hydraulic retention times was between 5.5 and 6.0 hours during the continuous flow studies.

TABLE 10-24

EFFECT OF INCREASED VOLATILITY ON BIODEGRADATION RATE COEFFICIENTS OF COMPOUNDS WITH THE SAME OVERALL REMOVALS

Compound	Removal (%)	k_v + (min^{-1})	k_b ++ (min^{-1})
Ethylbenzene	80	0.086	0.35
Toluene	80	0.078	0.32
Benzene	80	0.074	0.31
o-Xylene	80	0.059	0.25
Chlorobenzene	80	0.050	0.21
1,2-Dichlorobenzene	80	0.026	0.03
Nitrobenzene	80	<0.001	0.02

+ Calculated by Equation 7-2 for a 4.0 liter/min aeration rate

++ Calculated by Equation 10-9 for a 5.5 hour $\bar{t}$

TABLE 10-25

EFFECT OF AERATION RATE ON THE BIODEGRADATION RATE COEFFICIENT OF BENZENE

($\bar{t}$ = 5.5 hr)

Removal (%)	Aeration Rate (ℓ/min)	k_v + (min^{-1})	k_b ++ (min^{-1})
85	3.5	0.065	0.39
85	4.0	0.074	0.44
85	4.5	0.084	0.49

+ Calculated by Equation 7-2
++ Calculated by Equation 10-9

TABLE 10-26

EFFECT OF HYDRAULIC RETENTION TIME ON THE BIODEGRADATION RATE COEFFICIENT OF BENZENE

(4.0 ℓ/min Aeration)

Removal (%)	$\bar{t}$ (hrs)	k_v + (min^{-1})	k_b ++ (min^{-1})
85	4.5	0.074	0.44
85	5.0	0.074	0.44
85	5.5	0.074	0.44
85	6.0	0.074	0.44
85	6.5	0.074	0.44

+ Calculated by Equation 7-2
++ Calculated by Equation 10-9

10.5.2. CMB Biodegradation Rate Studies

Completely-mixed batch biodegradation rate studies were conducted with and without aeration as detailed in Section 5. These studies were conducted for two purposes: i) to confirm that the disappearances of the toxic organic compounds observed in the CMF bioreactors were due to biodegradation; and, ii) to independently measure biodegradation rate coefficients for selected organic compounds. Batch degradation studies were conducted with the biodegradable compounds benzene, toluene, ethylbenzene, chlorobenzene, and nitrobenzene.

10.5.2.1. Non-aerated CMB Biodegradation Studies

Batch biodegradation rate studies were conducted without aeration to study the biodegradation of microgram-per-liter concentrations of the volatile compounds benzene, chlorobenzene, and ethylbenzene. A 2.6-liter glass reactor equipped with a lid was used for the batch rate studies, and mixing was accomplished with a magnetic stir bar. Descriptions of the experimental system and procedures were given in Section 5.

Data from the CMB biodegradation rate studies without aeration was modeled as an overall first order removal process which can be described by

$$-\frac{dC}{dt} = k_bC \qquad (10\text{-}10)$$

Values of k_b, the biodegradation rate coefficient, were obtained from the slope of the least-squares linear regression line for data plotted as the logarithm of concentration versus time.

An initial series of control studies were conducted in deionized distilled water to evaluate what effect volatilization and adsorption onto the walls of the batch reactor had on the removal of each compound from the 2.6ℓ CMB reactor. Control studies were conducted under the same conditions as the biodegradation studies with activated sludge. Results of those studies showed negligible removal attributable to volatilization and adsorption onto the reactor. A second set of background studies was conducted with activated sludge treated with $HgCl_2$ to inhibit biological activitiy, as measured by dissolved oxygen uptake. These studies were conducted with three compounds: benzene, ethylbenzene and chlorobenzene. Initial concentrations were between 40 and 65 μg/ℓ, and the test results showed no measurable change in the aqueous concentration of each compound over the thirty minute sample period. This finding indicated that sorption of the biodegradable compounds by the activated sludge biomass was not significant and would not affect the aqueous concentration.

Results from four benzene studies, three toluene studies, one ethylbenzene study and one chlorobenzene study are presented in Figures 10-72 through 10-80. Each figure is a semi-logarithmic plot of concentration versus time data from one non-aerated, biodegradation rate study with activated sludge from an acclimated activated sludge bioreactor. Following each figure is a summary of the results, Tables 10-27 through 10-35, from the biodegradation study, operating conditions for the bioreactor from which the activated sludge was obtained, and a comparison of measured effluent and off-gas concentrations to concentrations predicted using the biodegradation rate coefficient determined in the batch biodegradation rate study. Predicted effluent and off-gas concentrations were calculated from equations described in Sections 7 and 9. The effluent concentration, C_e, was calculated by

$$C_e = \frac{C_i}{1+[(Q_g L+k_{v,o})+k_b]\bar{t}} \qquad (10\text{-}11)$$

in which the aeration rate, Q_a, is equal to the off-gas flow rate Q_g. The off-gas concentration, C_g, was calculated by

$$C_g = \frac{C_i(Q_g L+k_{v,o})V/Q_g}{1+[(Q_g L+k_{v,o})+k_b]\bar{t}} \qquad (10\text{-}12)$$

Overall removals were determined from a CMF reactor mass balance approach

$$\text{Removal (\%)} = 1 - \frac{C_e Q_e + C_g Q_g}{Q_i C_i} \times 100 \qquad (10\text{-}13)$$

in which $Q_i = Q_e$. An overall summary of the biodegradation rate coefficients from the non-aerated CMB biodegradation studies is presented by Table 10-36.

The four biodegradation rate studies in Figures 10-72 through 10-75 for benzene show that the first order removal rate model adequately described the biodegradation data. Least squares linear regression coefficients ranged from 0.978 to 0.995. Removal of benzene was very rapid in each case with a 50% reduction in concentration occurring within approximately five minutes. The background TOC in each case was between 12 and 18 mg/ℓ and represented the effluent TOC from the bioreactor from which the acclimated sludge was withdrawn.

Biodegradation rate coefficients for benzene measured in the batch degradation studies were nearly identical to the rate coefficients calculated from a CMF reactor mass balance using measured influent, effluent, and off-gas concentrations. As shown in Tables 10-27 through

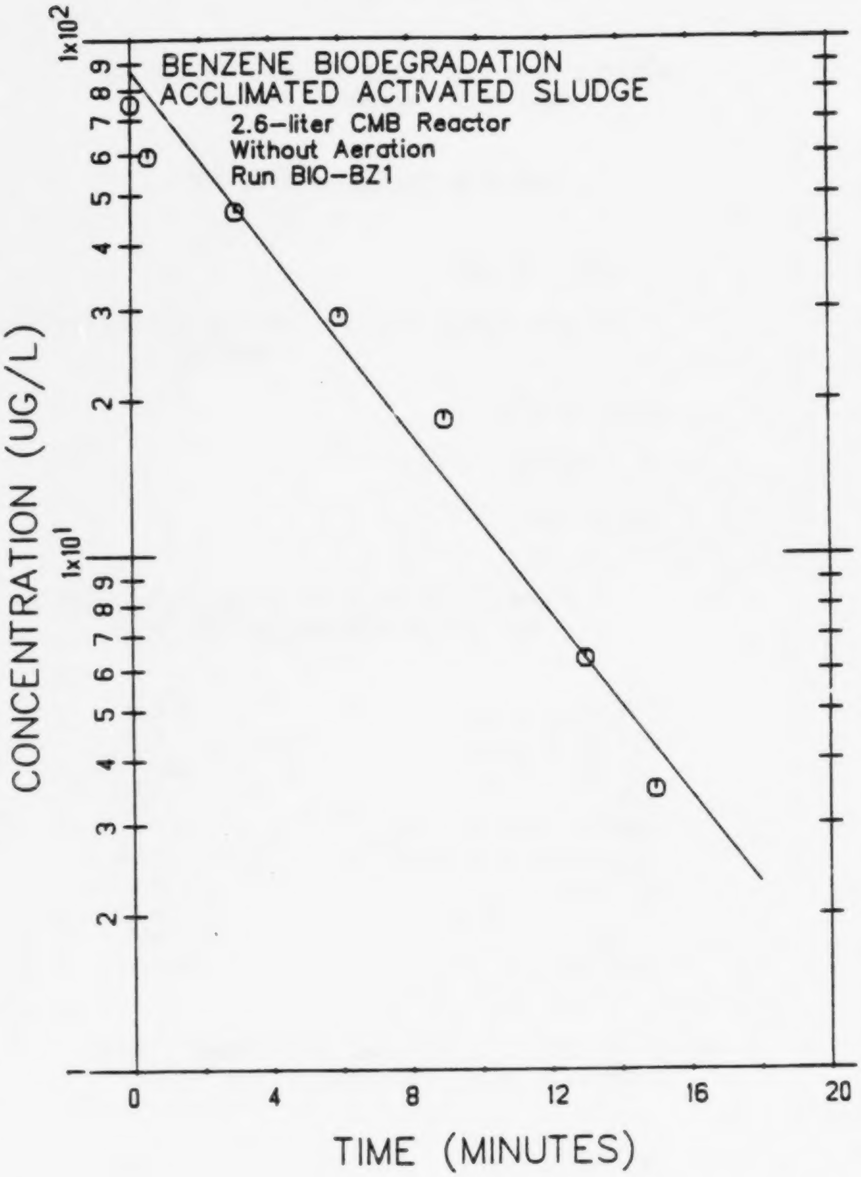


FIGURE 10-72. Experimental data and best-fit line describing benzene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge from the 6-day SRT benzene bioreactor study.)

TABLE 10-27

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO-BZ1

k_b ($\min^{-1}$): 0.224

Corr. Coef.: 0.978

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	116.2
Effluent (μg/l)	0.5
Off-Gas (ng/l)	197
N/N_o	0.23
Overall Removal (%)	77
k_b, Calculated ($\min^{-1}$)	0.26
k_v ($\min^{-1}$)	0.074
Q_a (liters/min)	4.0
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3440

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	1.2
Off-Gas (ng/l)	215
N/N_o	0.26
Overall Removal (%)	74

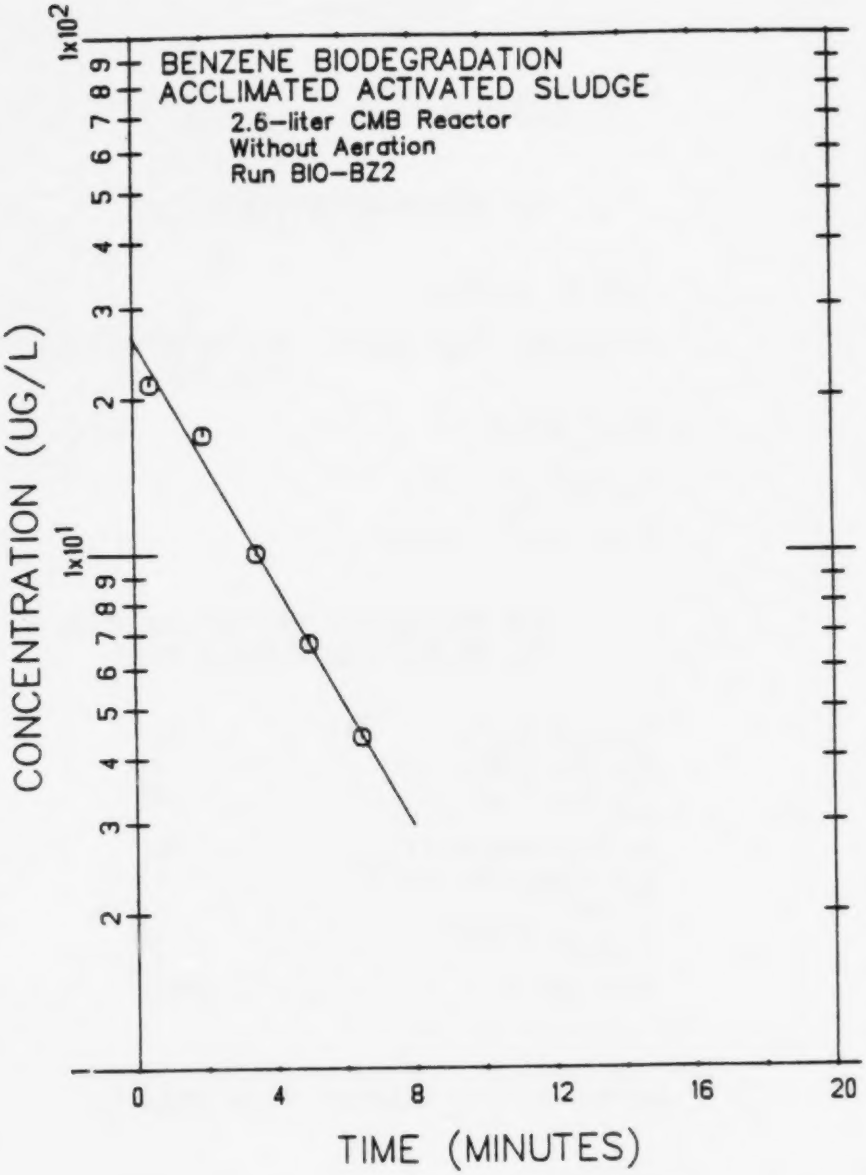


FIGURE 10-73. Experimental data and best-fit line describing benzene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge from the 6-day SRT bioreactor study with benzene.)

TABLE 10-28

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO-BZ2

k_b (min^{-1}): 0.28

Corr. Coef.: 0.995

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent ($\mu g/l$)	516.9
Effluent ($\mu g/l$)	3.4
Off-Gas (ng/l)	617
N/N_o	0.17
Overall Removal (%)	83
k_b, Calculated (min^{-1})	0.39
k_v (min^{-1})	0.076
Q_a (liters/min)	4.1
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3760

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent ($\mu g/l$)	4.3
Off-Gas (ng/l)	802
N/N_o	0.22
Overall Removal (%)	78

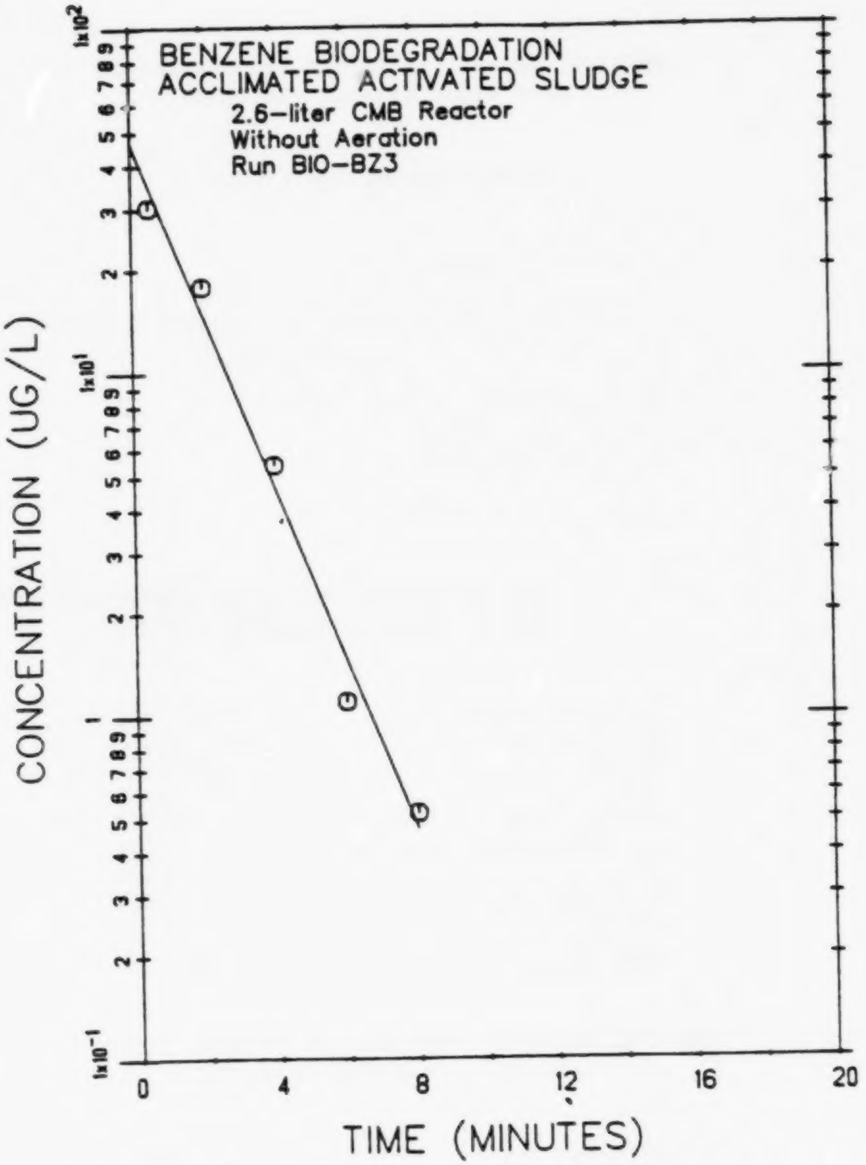


FIGURE 10-74. Experimental data and best-fit line describing benzene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge was from the 6-day SRT bioreactor study with benzene.)

TABLE 10-29

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO-BZ3

k_b (min^{-1}): 0.58

Corr. Coef.: 0.993

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	140.2
Effluent (μg/l)	0.5
Off-Gas (ng/l)	112
N/N_o	0.11
Overall Removal (%)	89
k_b, Calculated (min^{-1})	0.62
k_v (min^{-1})	0.074
Q_a (liters/min)	4.0
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3310

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	0.6
Off-Gas (ng/l)	111
N/N_o	0.12
Overall Removal (%)	88

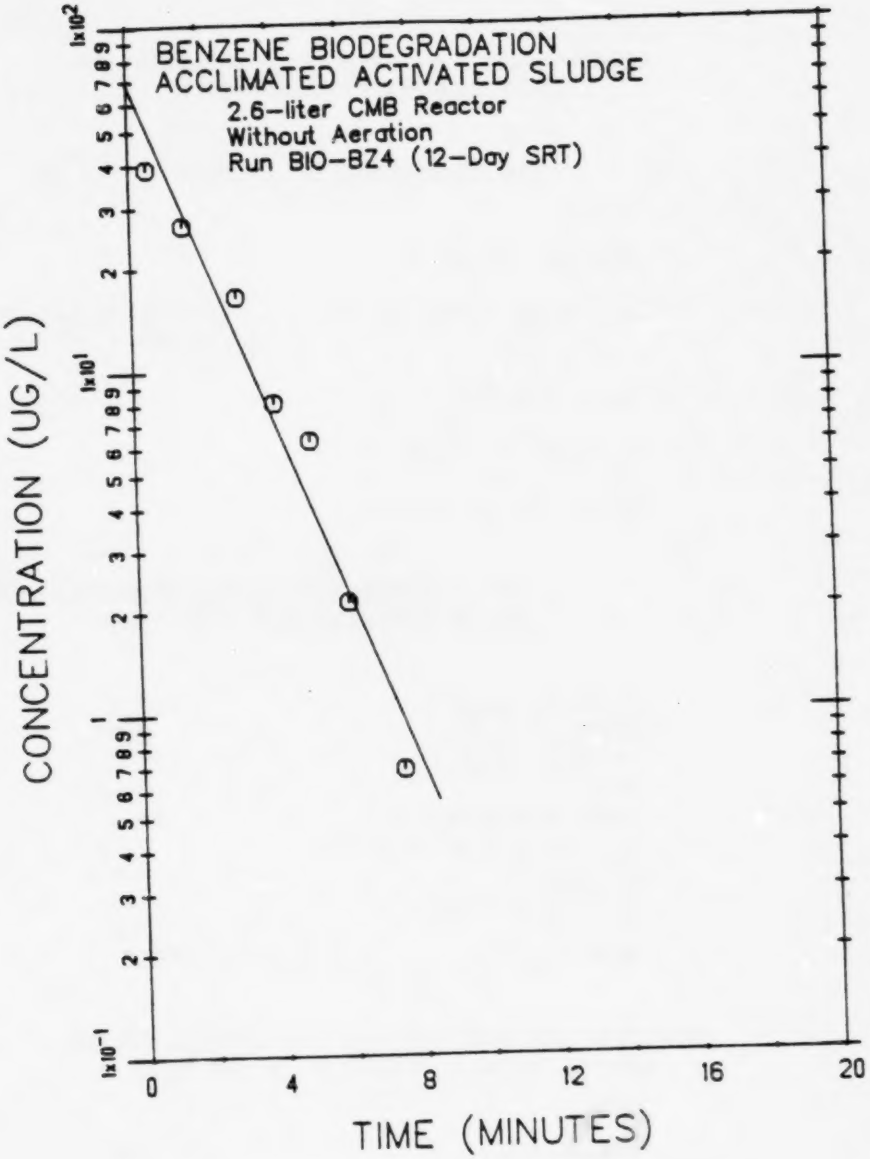


FIGURE 10-75. Experimental data and best-fit line describing benzene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge was from the 12-day SRT biorector study with benzene.)

TABLE 10-30

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Acclimated Activated Sludge
12-day SRT

Run: BIO-BZ4

k_b (min^{-1}): 0.57

Corr. Coef.: 0.979

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	112.2
Effluent (μg/l)	0.3
Off-Gas (ng/l)	91
N/N_o	0.11
Overall Removal (%)	89
k_b, Calculated (min^{-1})	0.55
k_v (min^{-1})	0.074
Q_a (liters/min)	3.5
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	5890

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	0.5
Off-Gas (ng/l)	97
N/N_o	0.12
Overall Removal (%)	88

10-30, there was quite good agreement between predicted and measured effluent and off-gas concentrations and overall removals. The similarity between predicted and observed values held for bioreactors receiving influent concentrations ranging from 100 to 500 μg/ℓ. Batch degradation studies B10-BZ1, B10-BZ3, and B10-BZ4 were conducted with activated sludge from acclimated activated sludge bioreactors receiving influent benzene concentrations averaging about 100 μg/ℓ. Study B10-BZ2 was performed with activated sludge from a bioreactor with influent concentrations between 500 and 550 μg/ℓ at the time the batch study was conducted.

Figures 10-74 and 10-75 are results of biodegradation rate studies with benzene run on consecutive days with acclimated sludge from 6-day and 12-day SRT bioreactors, respectively. As previously described the overall removal of benzene from the 6 and 12-day SRT units was similar. The biodegradation rate coefficients for the 6 and 12-day SRT activated sludges measured in the 2.6-liter CMB reactor studies were approximately the same, confirming the similarity in biodegradative benzene removal observed in the CMF bioreactors.

Results of three toluene biodegradation rate studies given by Figures 10-76 through 10-78 are summarized in Tables 10-31 through 10-33, respectively. All three batch degradation studies were conducted with activated sludge from the same 6-day SRT activated sludge unit. Study B10-TOL1, Figure 10-76 and Table 10-31, was conducted at the end of the acclimation phase, and study B10-TOL2, Figure 10-77 and Table 10-32, was conducted well into steady-state toluene biodegradation phase. Agreement between measured and calculated toluene biodegradation rate coefficients was not as good as occurred for benzene. In the first rate study the measured value was only about one-half the coefficient value calculated from the CMF bioreactor data. As a result, the amount of toluene predicted to be degraded was only 65% compared with a measured value of 76%. Agreement between the rate coefficient calculated from the CMF bioreactor data and the measured value obtained in the CMB reactor was better in the second biodegradation rate study. The measured value was 0.26 min^{-1}. The model predicted effluent and off-gas concentrations of 0.7 μg/ℓ and 139 ng/ℓ, respectively, while the observed values were 0.6 μg/ℓ and 96 ng/ℓ, respectively. Although the value of k_b differed by more than 30% the difference between predicted and observed overall removals, 76% and 82%, respectively, was small. The reason that considerably different k_b values can result in similar overall removals is attributable to the character of the first-order removal mode. Overall removals in the 76 to 82% range fall on that portion of the exponential curve relating k_b to overall removal where large incremental increases in k_b are required to effect small increases in percent removal.

Data presented in Figure 10-78 and Table 10-33 were obtained during a temporary upset period in the activated sludge bioreactor. The overall toluene removal measured in the bioreactor on the day the batch degradation study was conducted was about 59%, resulting in a calculated biodegradation rate coefficient of 0.116 min^{-1}. Data from Table 10-15 indicates that removal of toluene averaged more than 83% over the steady-state operating period. Results from the batch degradation study

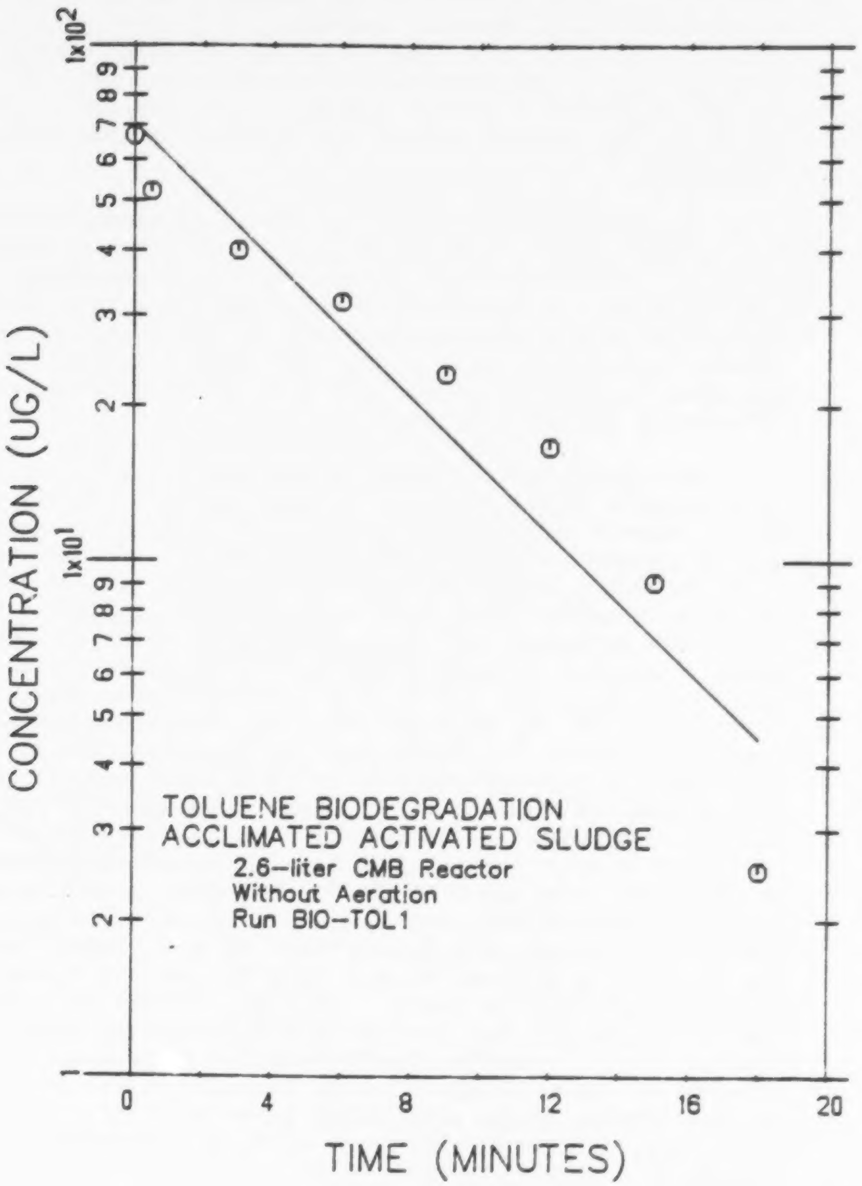


FIGURE 10-76. Experimental data and best-fit line describing toluene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge was from the 6-day SRT bioreactor study with toluene.)

TABLE 10-31

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Toluene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO-TOL1

k_b (min^{-1}): 0.15

Corr. Coef.: 0.956

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent ($\mu g/l$)	98.1
Effluent ($\mu g/l$)	0.4
Off-Gas (ng/l)	170
N/N_o	0.24
Overall Removal (%)	76
k_b, Calculated (min^{-1})	0.26
k_v (min^{-1})	0.078
Q_a (liters/min)	4.0
t (hrs)	5.6
MLSS (mg/l)	3250

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent ($\mu g/l$)	1.3
Off-Gas (ng/l)	247
N/N_o	0.35
Overall Removal (%)	65

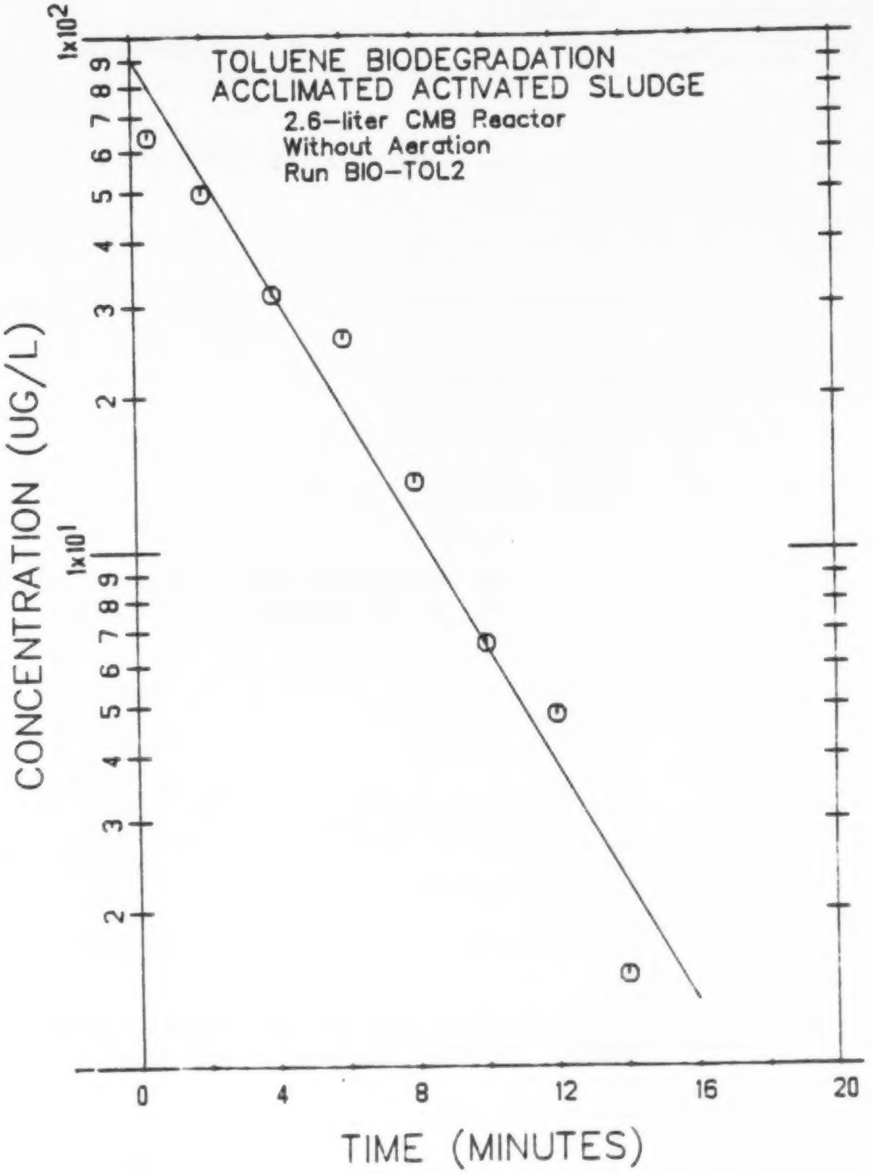


FIGURE 10-77. Experimental data and best-fit line describing toluene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge was from the 6-day SRT bioreactor study with toluene.)

TABLE 10-32

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Toluene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO-TOL2

k_b (min^{-1}): 0.26

Corr. Coef.: 0.982

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	85.7
Effluent (μg/l)	0.6
Off-Gas (ng/l)	96
N/N_o	0.18
Overall Removal (%)	82
k_b, Calculated (min^{-1})	0.38
k_v (min^{-1})	0.079
Q_a (liters/min)	4.1
t (hrs)	5.7
MLSS (mg/l)	3170

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	0.7
Off-Gas (ng/l)	139
N/N_o	0.24
Overall Removal (%)	76

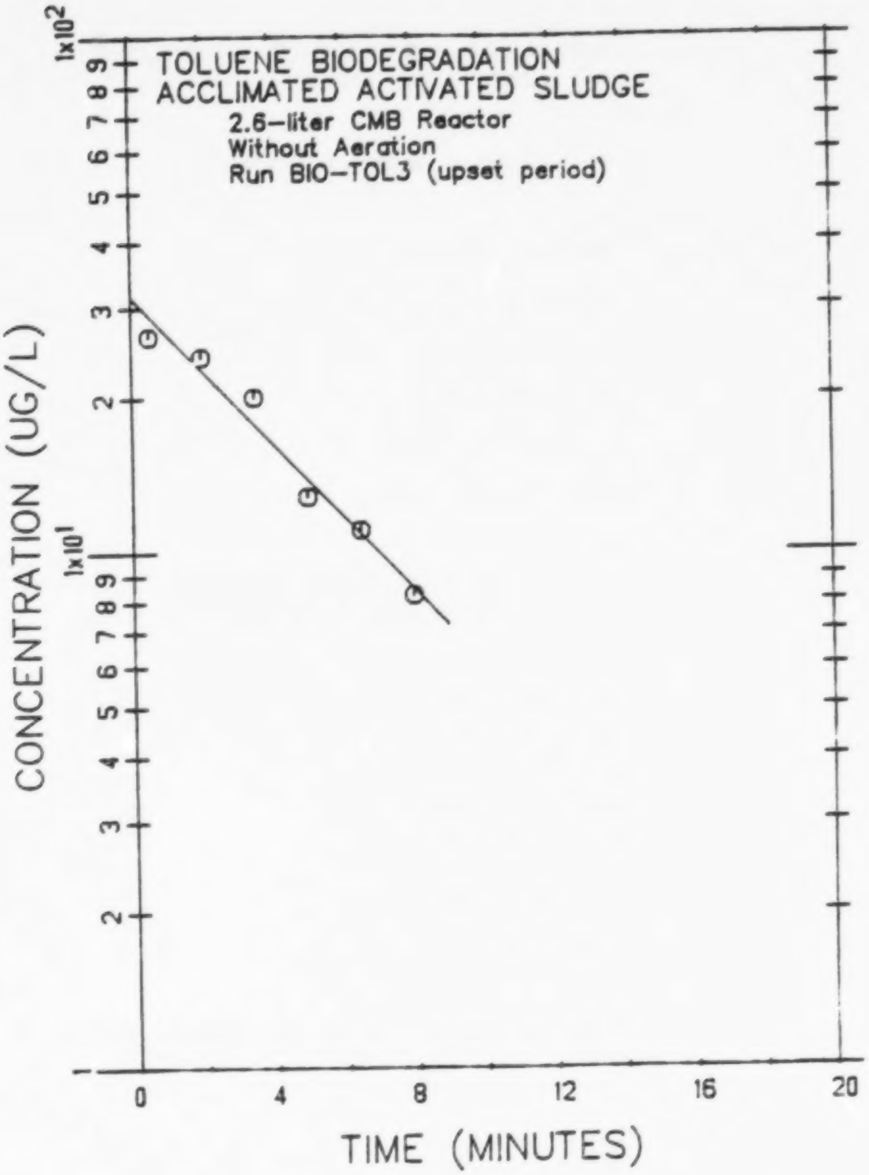


FIGURE 10-78. Experimental data and best-fit line describing toluene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge was taken during an upset period in the 6-day SRT bioreactor study with toluene.)

TABLE 10-33

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Toluene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT (Upset Period)

Run: BIO-TOL3

k_b (min^{-1}): 0.164

Corr. Coef.: 0.984

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	100.6
Effluent (μg/l)	1.1
Off-Gas (ng/l)	301
N/N_o	0.409
Overall Removal (%)	59
k_b, Calculated (min^{-1})	0.116
k_v (min^{-1})	0.078
Q_a (liters/min)	4.0
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3540

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	1.2
Off-Gas (ng/l)	238
N/N_o	0.33
Overall Removal (%)	67

yielded a rate coefficient of 0.164 min^{-1}. Effluent and off-gas concentrations predicted for $k_b = 0.164\ min^{-1}$ were 1.2 µg/ℓ and 238 ng/ℓ, respectively, which compared favorably with the measured values of 1.1 µg/ℓ and 301 ng/ℓ. The predicted overall removal of 67% was slightly larger than the measured 59%.

Results of the ethylbenzene biodegradation rate study are given by Figure 10-79 and Table 10-34. The activated sludge was from a well-acclimated bioreactor that had been receiving ethylbenzene for over thirty days. The overall ethylbenzene removal on the day the rate study was run was 82%; the mean value for the whole study was 81%. As shown by Figure 10-79, the first order model adequately described ethylbenzene removal in the biodegradation study and gave a rate coefficient of 0.35 min^{-1}. The biodegradation rate coefficient calculated from a CMF reactor mass balance was slightly larger, 0.42 min^{-1}. Predicted and measured overall removals were approximately the same; 79 and 82%, respectively.

The results from the chlorobenzene biodegradation rate study are plotted in Figure 10-80 and summarized in Table 10-35. The well-acclimated sludge was obtained from the steady-state operating period of the 6-day SRT chlorobenzene activated sludge study previously reported. The overall chlorobenzene removal of 87% measured on the day the biodegradation study was conducted was larger than the average value for the whole study, 82%. As shown in Figure 10-80 the biodegradation rate data fit the first order removal model, giving a biodegradation rate coefficient of 0.23 min^{-1}. The value calculated from a CMF reactor mass balance approach was 0.36 min^{-1}. While the measured removal of chlorobenzene by biodegradation on the day of the rate study was somewhat larger than the value predicted by the 0.23 min^{-1} rate coefficient, 87% compared to 81%, respectively, the predicted value was almost identical to the average removal observed during the steady-state biodegradation period, 82%. The comparison of model predicted and measured effluent and off-gas concentrations in Table 10-35 shows that the model provided an adequate indication of bioreactor performance with respect to chlorobenzene removal.

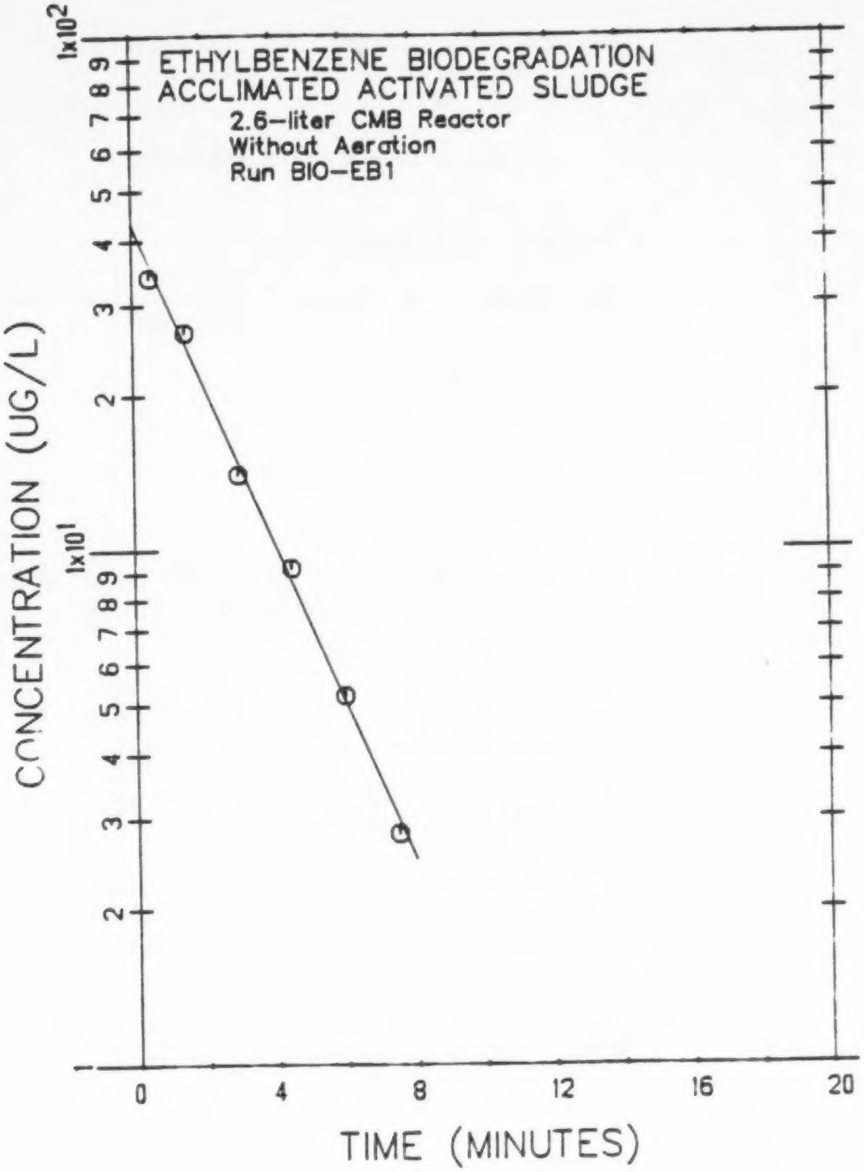


FIGURE 10-79. Experimental data and best-fit line describing ethylbenzene biodegradation by acclimated sludge in a completely-mixed batch (CMB) reactor activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge was from the 6-day SRT bioreactor study with ethylbenzene.)

TABLE 10-34

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Ethylbenzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO-EB1

k_b (min^{-1}): 0.35

Corr. Coef.: 0.990

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	120.0
Effluent (μg/l)	0.6
Off-Gas (ng/l)	160
N/N_o	0.18
Overall Removal (%)	82
k_b, Calculated (min^{-1})	0.42
k_v (min^{-1})	0.092
Q_a (liters/min)	4.4
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3290

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	0.8
Off-Gas (ng/l)	174
N/N_o	0.21
Overall Removal (%)	79

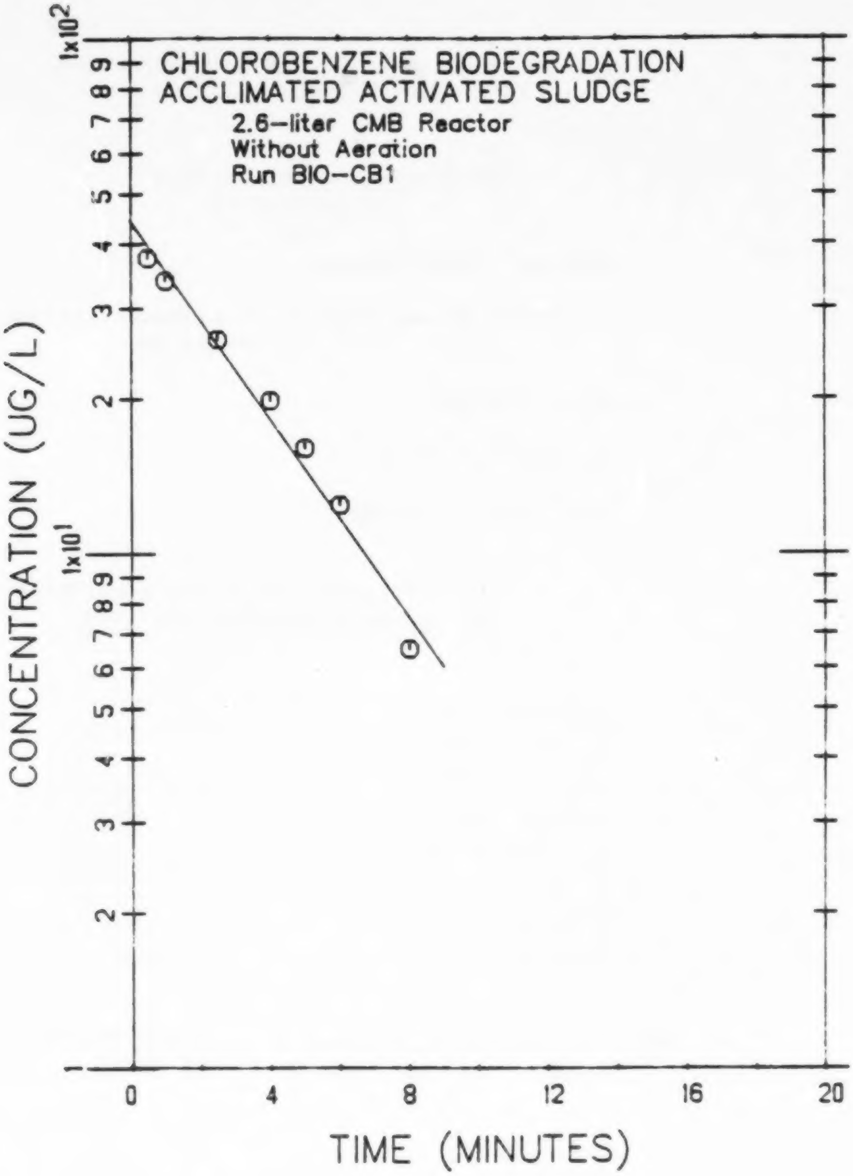


FIGURE 10-80. Experimental data and best-fit line describing chlorobenzene biodegradation by acclimated activated sludge in a completely-mixed batch (CMB) reactor without aeration. (Activated sludge was from the 6-day SRT bioreactor study with chlorobenzene.)

TABLE 10-35

RESULTS FROM 2.6-LITER CMB BIODEGRADATION RATE STUDY WITHOUT AERATION

CMB BIODEGRADATION RESULTS

Solute: Chlorobenzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO-CB1

k_b (min^{-1}): 0.23

Corr. Coef.: 0.989

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	110.0
Effluent (μg/l)	0.6
Off-Gas (ng/l)	93
N/N_o	0.127
Overall Removal (%)	87.3
k_b, Calculated (min-1)	0.36
kv (min-1)	0.050
Qa (liters/min)	4.0
$\bar{t}$ (hrs)	6.0
MLSS (mg/l)	3780

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING kb MEASURED IN CMB STUDY

Effluent (μg/l)	1.1
Off-Gas (ng/l)	140
N/No	0.192
Overall Removal (%)	80.8

TABLE 10-36

SUMMARY OF k_b VALUES MEASURED IN CMB DEGRADATION STUDIES, AND COMPARISON OF OVERALL % REMOVALS MEASURED IN CMF BIOREACTORS AND PREDICTED FROM k_b VALUES MEASURED IN 2.6 LITER CMB DEGRADATION STUDIES

Compound	k_b (min^{-1})	Overall Removals (%) Measured	 Predicted
Benzene	0.22	77	74
	0.28	83	78
	0.58	89	88
	0.57	89	88
Toluene	0.15	76	65
	0.26	82	76
	0.16	59	67
Chlorobenzene	0.23	87	81
Ethylbenzene	0.35	82	79

10.5.2.2. Aerated CMB Biodegradation Studies

A second type of biodegradation study was conducted with acclimated activated sludge to measure the rate of removal of selected compounds from the 10-liter activated sludge bioreactors operated in batch modes with aeration. The continuous flow bioreactors were converted to batch reactors by temporarily stopping influent and sludge waste flows. A complete description of the experimental procedures was given in Section 5.

Reductions in the aqueous concentrations of organic compounds in 10-liter CMB aerated activated sludge bioreactors resulting from biodegradation and volatilization can be described by the first order expression:

$$-\frac{dC}{dt} = k_v C + k_b C \tag{10-14}$$

Upon integration Equation 10-14 can be written in the linearized form

$$\ell n\ C = \ell n\ C_i - (k_v + k_b)t \tag{10-15}$$

A plot of logarithm of concentration versus time, t, yields a slope equal to the overall removal rate coefficient, k_o, which represents the sum of the biodegradation, k_b, and volatilization, k_v, removal rate coefficients, as described by Equation 10-16

$$k_o = k_v + k_b \tag{10-16}$$

Results from the batch volatilization studies demonstrated that k_v could be calculated for any aeration rate by the relationship

$$k_v = k_{v,o} + LQ_a \tag{10-17}$$

The biodegradation rate coefficient, k_b, was calculated using the slope of the best fit linear regression line through the data from the aerated biodegradation studies, k_o, and the value of k_v calculated from the aeration rate, calculated as follows:

$$k_b = k_o - (LQ_a + k_{v,o}) \tag{10-18}$$

Aerated 10-liter CMB biodegradation studies were conducted with three volatile, biodegradable compounds: benzene, toluene, and chlorobenzene. Initial toxics concentrations ranged from approximately 20 to 100 μg/ℓ. Results from the aerated CMB are given in Figures 10-81 through 10-86. Following each figure is a table containing a summary of results from the rate study and operating conditions for the bioreactor in which the study was conducted. An overall summary of results from the aerated CMB biodegradation rate studies is presented by Table 10-46.

Results from biodegradation studies with benzene are presented in Figures 10-81 through 10-84 and summarized by Tables 10-37 through 10-40. The first three rate studies (identified by B10+AIR-BZ1, B10+AIR-BZ2, and B10+AIR-BZ3) were conducted in the same activated sludge bioreactor. B10+AIR-BZ1 was run during the second week of the acclimation phase while the other two studies were conducted during the steady-state benzene biodegradation phase. The fourth biodegradation rate study (B10+AIR-BZ4) was conducted during the multi-solute activated sludge study, described in Section 10-6, when the influent benzene concentration was between 400 and 500 μg/ℓ.

The data from the aerated, biodegradation rate studies with benzene fit the first-order overall removal model as evidenced by linear regression coefficients, r^2, which ranged from 0.997 to 0.999. As shown by Tables 10-37 through 10-40, the overall removal rate coefficient, k_o, was significantly larger than the volatilization rate coefficient, k_v, calculated by $k_v = k_{v,o} + LQ_a$ for the aeration rate used in the batch study. The rate study conducted during the acclimation phase yielded the smallest biodegradation rate coefficient, 0.10 min^{-1}. The two biodegradation rate coefficients measured during the relatively steady-state benzene removal period were significantly larger and approximately the same, 0.36 and 0.40 min^{-1}. Measured effluent and off-gas benzene concentrations were successfully predicted using biodegradation rate coefficients obtained from the batch biodegradation rate experiments, as indicated by the comparisons of measured and predicted experiments, in Tables 10-37, 10-38, and 10-39. The ratio of predicted to measured overall removals ranged from 0.85 to 1.09 for the three rate studies.

The fourth batch biodegradation study yielded an overall removal rate coefficient, k_o, of 0.582 min^{-1}. The volatilization rate coefficient, k_v, was calculated to be 0.084 min^{-1} based upon the 4.5 ℓ/min aeration rate. Subtracting k_v from k_o gave a biodegradation rate coefficient, k_b, of 0.498 min^{-1}. The ratio k_b/k_v was approximately 6.0 in the batch study as volatilization accounted for less than 15% of the value of k_o; the rest was attributed to biodegradation. Predicted and measured overall benzene removal in the CMF bioreactor on the day the batch degradation study was run were 87 and 89%, respectively.

Results from an aerated biodegradation study with toluene were not plotted, but are summarized by Table 10-41. The overall rate coefficient for the batch study of 0.434 min^{-1} was composed of volatilization and biodegradation components of 0.081 and 0.353 min^{-1}, respectively. The aerated biodegradation study was conducted in the toluene 6-day SRT activated sludge bioreactor described in Section 10.4.

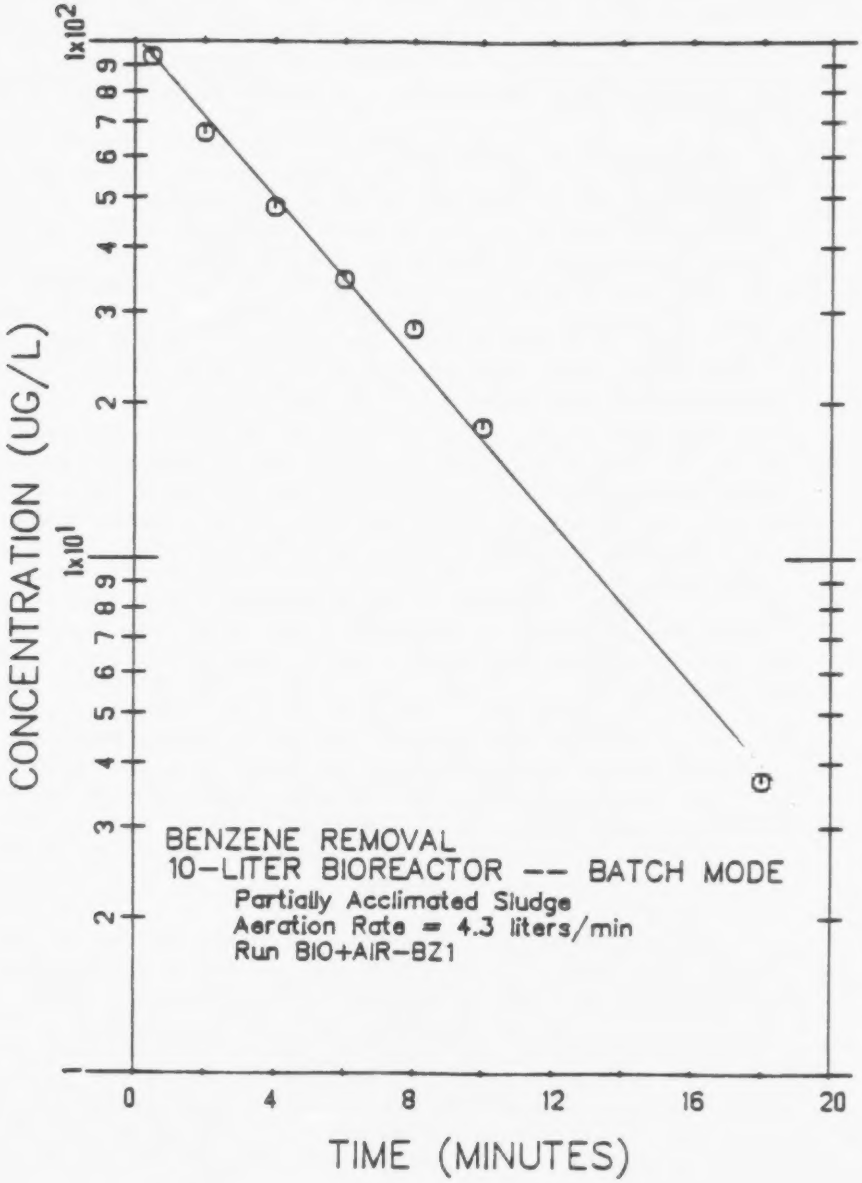


FIGURE 10-81. Experimental data and best-fit line describing benzene removal by biodegradation and volatilization during a completely-mixed batch rate study in a 10-liter bioreactor with a 4.3-liter/min aeration rate. (Study was conducted with the benzene 6-day SRT activated sludge bioreactor.)

TABLE 10-37

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Partially Acclimated Sludge
6-day SRT

Run: BIO+AIR-BZ1

k_o (min^{-1}): 0.179

Corr. Coef.: 0.998

k_v (min^{-1}): 0.079 (Q_a = 4.3 l/min)

k_b (min^{-1}): 0.10

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	86.2
Effluent (μg/l)	1.2
Off-Gas (ng/l)	209
N/N_o	0.35
Overall Removal (%)	65
k_b, Calculated (min^{-1})	0.154
k_v (min^{-1})	0.080
Q_a (liters/min)	4.3
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	2850

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	1.4
Off-Gas (ng/l)	268
N/N_o	0.448
Overall Removal (%)	55.2

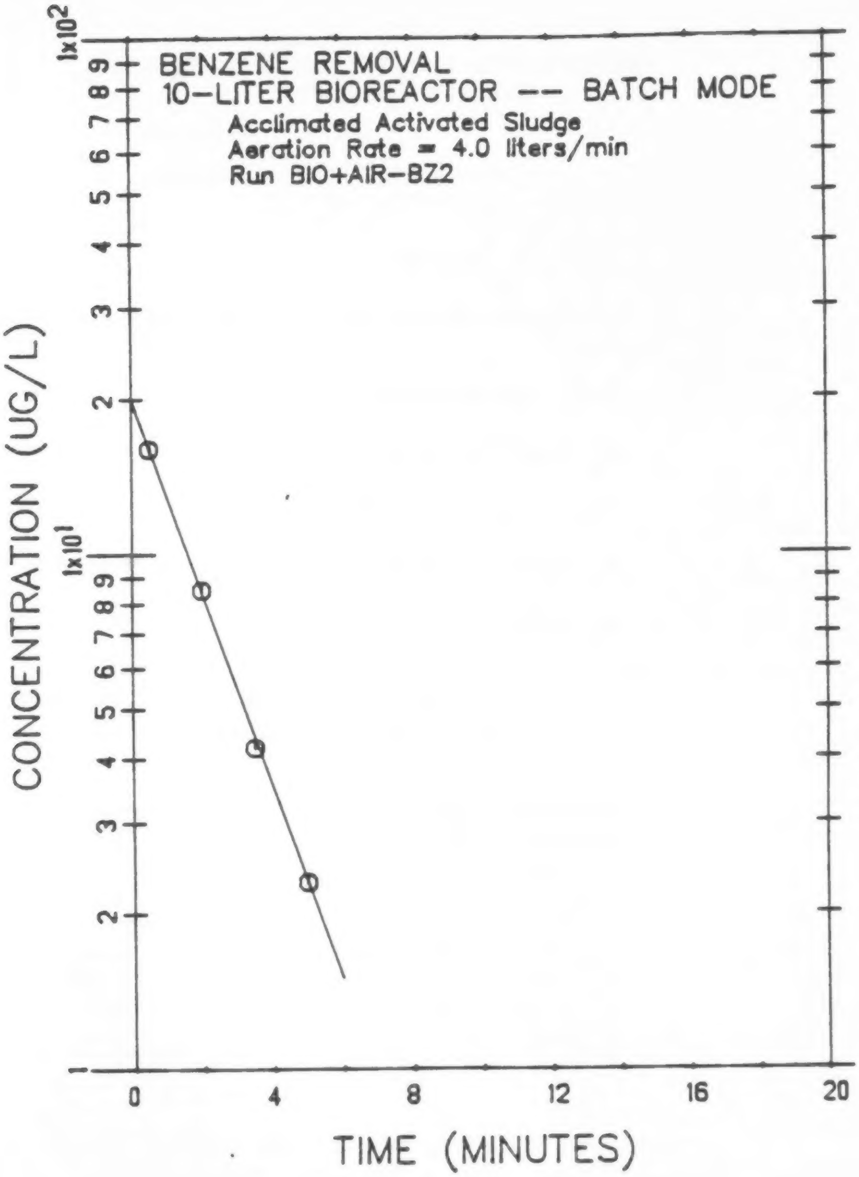


FIGURE 10-82. Experimental data and best-fit line describing benzene removal by biodegradation and volatilization during a completely-mixed batch rate study in a 10-liter activated sludge bioreactor with a 4.0-liter/min aeration rate. (Study was conducted with the benzene 6-day SRT activated sludge bioreactor.)

TABLE 10-38

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO+AIR-BZ2

k_o (min^{-1}): 0.436

Corr. Coef.: 0.999

k_v (min^{-1}): 0.074 (Q_a = 4.0 l/min)

k_b (min^{-1}): 0.361

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	187
Effluent (μg/l)	0.8
Off-Gas (ng/l)	334
N/N_o	0.247
Overall Removal (%)	75.3
k_b, Calculated (min^{-1})	0.236
k_v (min^{-1})	0.074
Q_a (liters/min)	4.0
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3360

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	1.3
Off-Gas (ng/l)	238
N/N_o	0.177
Overall Removal (%)	82.3

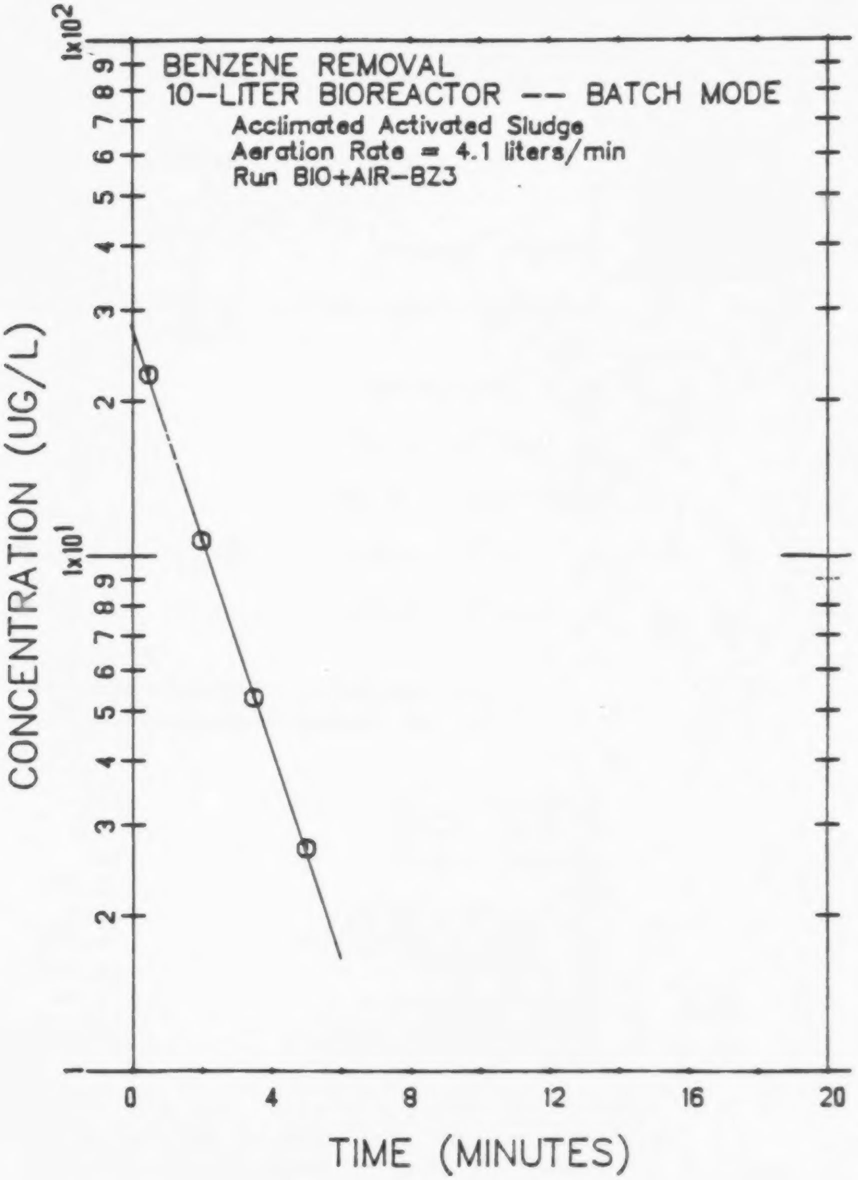


FIGURE 10-83. Experimental data and best-fit line describing benzene removal by biodegradation and volatilization during a completely-mixed batch rate study in a 10-liter activated sludge bioreactor with a 4.1-liter/min aeration rate. (Study was conducted with the benzene 6-day SRT activated sludge bioreactor.)

TABLE 10-39

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO+AIR-BZ3

k_o ($\min^{-1}$): 0.471

Corr. Coef.: 0.999

k_v ($\min^{-1}$): 0.076 (Q_a = 4.1 l/min)

k_b ($\min^{-1}$): 0.395

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	155
Effluent (μg/l)	0.6
Off-Gas (ng/l)	224
N/N_o	0.193
Overall Removal (%)	80.7
k_b, Calculated ($\min^{-1}$)	0.308
k_v ($\min^{-1}$)	0.071
Q_a (liters/min)	3.8
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3410

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	1.0
Off-Gas (ng/l)	179
N/N_o	0.157
Overall Removal (%)	84.3

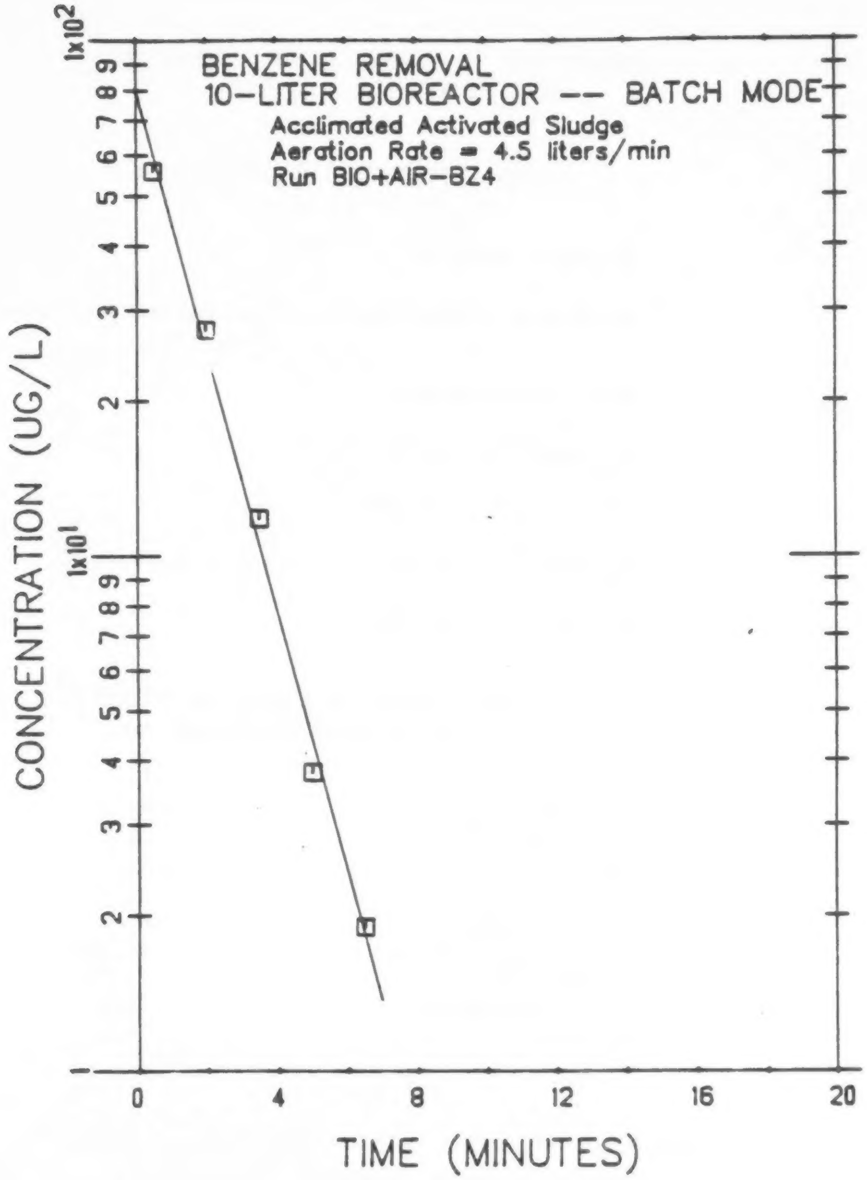


FIGURE 10-84. Experimental data and best-fit line describing benzene removal by biodegradation and volatilization during a completely-mixed batch rate study in a 10-liter activated sludge bioreactor with a 4.5-liter/min aeration rate. (Study was conducted with the benzene 6-day SRT activated sludge bioreactor.)

TABLE 10-40

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO+AIR-BZ4

k_o (min^{-1}): 0.582

Corr. Coef.: 0.997

k_v (min^{-1}): 0.084 (Q_a = 4.5 l/min)

k_b (min^{-1}): 0.498

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	432
Effluent (μg/l)	0.9
Off-Gas (ng/l)	362
N/N_o	0.115
Overall Removal (%)	88.5
k_b, Calculated (min^{-1})	0.582
k_v (min^{-1})	0.073
Q_a (liters/min)	3.9
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3700

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	2.3
Off-Gas (ng/l)	420
N/N_o	0.132
Overall Removal (%)	86.8

TABLE 10-41

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Toluene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO+AIR-TOL

k_o (min^{-1}): 0.434

Corr. Coef.: 0.998

k_v (min^{-1}): 0.081 (Q_a = 4.2 l/min)

k_b (min^{-1}): 0.353

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	117
Effluent (μg/l)	0.6
Off-Gas (ng/l)	139
N/N_o	0.163
Overall Removal (%)	83.7
k_b, Calculated (min^{-1})	0.41
k_v (min^{-1})	0.078
Q_a (liters/min)	4.0
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3550

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	0.8
Off-Gas (ng/l)	157
N/N_o	0.186
Overall Removal (%)	81.4

The batch measured biodegradation rate coefficient, 0.353 min^{-1}, compared favorably with both the value calculated from toluene bioreactor concentration data measured the day of the CMB rate study, 0.41 min^{-1}, and the degradation rate coefficient averaged during toluene steady state removal periods, 0.45 min^{-1}.

Tables 10-42 and 10-43 summarize results of chlorobenzene aerated biodegradation rate studies plotted in linearized form in Figures 10-85 and 10-86, respectively. The first rate study was conducted during the steady state chlorobenzene removal phase of the 6-day SRT activated sludge study. An overall removal rate coefficient of 0.333 min^{-1} was measured and used to calculate the biodegradation rate coefficient, 0.28 min^{-1}. The rate coefficient obtained from the batch study was approximately the same as the value calculated from a CMF reactor mass balance, 0.30 min^{-1}, on the day the rate study was run. The mean biodegradation rate coefficient observed during the chlorobenzene activated sludge study was 0.26 min^{-1}. Predicted and measured overall chlorobenzene removals for the day of the aerated biodegradation rate study were not significantly different, 86 and 87%, respectively.

The second aerated biodegradation study with chlorobenzene was conducted on Day 61 of the multi-solute activated sludge study described in Section 10.6. Biodegradation and volatilization rate coefficients of 0.43 and 0.053 min^{-1}, respectively, were obtained from the overall removal coefficient, 0.48 min^{-1}, measured in the batch study. Using the value of k_b measured in the batch rate study, the model predicted a 90% removal of chlorobenzene due to biodegradation compared with the observed 83% degradation on the day of the rate study.

Two aerated biodegradation rate studies were conducted with nitrobenzene in well-acclimated 10-liter bioreactors operated in batch modes. Results from the first rate study are summarized by Table 10-44. This study was conducted during the steady-state nitrobenzene degradation period of a 6-day SRT bioreactor receiving an influent nitrobenzene concentration of approximately 100 μg/ℓ. An overall removal rate coefficient of 0.09 min^{-1} was calculated for the batch reactor. Since nitrobenzene was only slightly volatile (k_v<0.001 min^{-1}) in the experimental system, the overall removal rate coefficient was considered a good estimate of the biodegradation rate coefficient. The value of k_b for nitrobenzene was significantly smaller than those measured for benzene, toluene, ethylbenzene, and chlorobenzene. While the measured biodegradation rate coefficient reported in Table 10-44 was less than the value calculated by Equation 10-9, it provided a relatively accurate prediction of the effluent concentration and overall removal of nitrobenzene from the CMF bioreactor.

The second aerated biodegradation study with nitrobenzene was conducted during the steady state operating period when the influent nitrobenzene concentration was approximately 1300μg/ℓ. The biodegradation rate coefficient measured during the batch rate study was 0.08 min^{-1}. Results from this biodegradation rate study are given in Table 10-45. Measured values were significantly less than predicted values for these conditions.

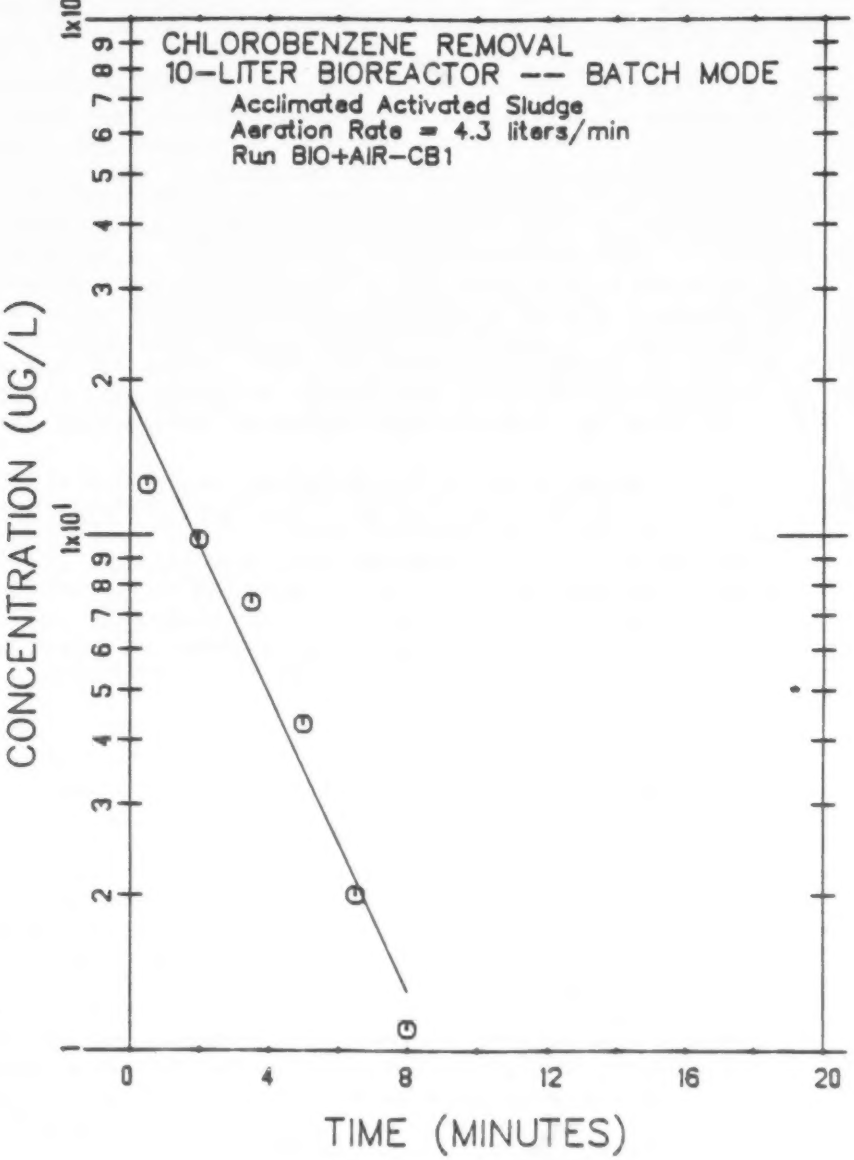


FIGURE 10-85. Experimental data and best-fit line describing chlorobenzene removal by biodegradation and volatilization during a completely-mixed batch rate study in a 10-liter activated sludge bioreactor with a 4.3 liter/min aeration rate. (Study was conducted with the chlorobenzene 6-day SRT activated sludge bioreactor.)

TABLE 10-42

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Chlorobenzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO+AIR-CB1

k_o (min^{-1}): 0.333

Corr. Coef.: 0.980

k_v (min^{-1}): 0.053 (Q_a = 4.3 l/min)

k_b (min^{-1}): 0.280

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	181
Effluent (μg/l)	2.4
Off-Gas (ng/l)	182
N/N_o	0.133
Overall Removal (%)	86.7
k_b, Calculated (min^{-1})	0.302
k_v (min^{-1})	0.043
Q_a (liters/min)	3.5
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3270

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	1.6
Off-Gas (ng/l)	203
N/N_o	0.142
Overall Removal (%)	85.8

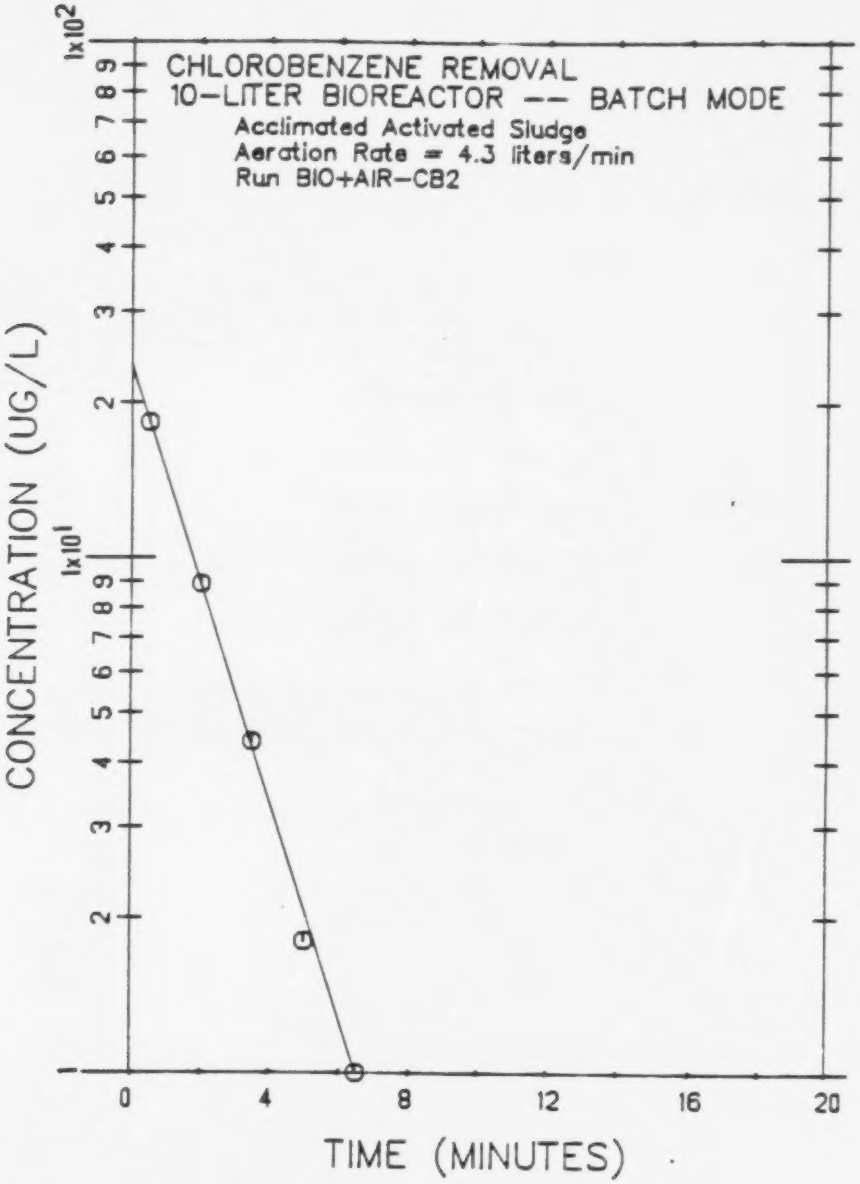


FIGURE 10-86. Experimental data and best-fit line describing chlorobenzene removal by biodegradation and volatilization during a completely-mixed batch rate study in a 10-liter activated sludge bioreactor with a 4.3 liter/min aeration rate. (Study was conducted with the chlorobenzene 6-day SRT activated sludge bioreactor.)

TABLE 10-43

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Chlorobenzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO+AIR-CB2

k_o (min^{-1}): 0.484

Corr. Coef.: 0.999

k_v (min^{-1}): 0.053 (Q_a = 4.3 l/min)

k_b (min^{-1}): 0.431

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	1820
Effluent (μg/l)	8.4
Off-Gas (ng/l)	2290
N/N_o	0.169
Overall Removal (%)	83.1
k_b, Calculated (min^{-1})	0.246
k_v (min^{-1})	0.047
Q_a (liters/min)	3.8
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3940

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	11.0
Off-Gas (μg/l)	1360
N/N_o	0.104
Overall Removal (%)	89.6

TABLE 10-44

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Nitrobenzene

Activated Sludge Source: Acclimated Activated Sludge
6-day SRT

Run: BIO+AIR-NB1

k_o (min^{-1}): 0.09

Corr. Coef.: 0.972

k_v (min^{-1}): <0.001 (Q_a = 4.2 l/min)

k_b (min^{-1}): 0.09

CMF BIOREACTOR OPERATING CONDITIONS ON THE DAY OF THE BIODEGRADATION STUDY

Influent (μg/l)	122
Effluent (μg/l)	2.5
Off-Gas (ng/l)	<20
N/N_o	0.02
Overall Removal (%)	98
k_b, Calculated (min^{-1})	0.18
k_v (min^{-1})	<0.001
Q_a (liters/min)	4.0
$\bar{t}$ (hrs)	5.6
MLSS (mg/l)	3630

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/l)	4.0
Off-Gas (ng/l)	30
N/N_o	0.04
Overall Removal (%)	96

TABLE 10-45

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Nitrobenzene
Run: B10 + Air - NB2
Activated Sludge Source: Acclimated Activated Sludge; 6-day SRT

k_o (min^{-1}): 0.08

Corr. Coef.: 0.973

k_v(min^{-1}): <0.001 (Q_a=4.0 ℓ/min)

k_b(min^{-1}): 0.08

AVERAGE CMF BIOREACTOR OPERATING CONDITIONS FOR THE DAY OF THE BIODEGRADATION RATE STUDY

$\bar{t}$ (hrs)	5.6
Influent (μg/ℓ)	1340
Effluent (μg/ℓ)	4.0
Off-Gas (ng/ℓ)	<50
N/N_o	0.01
Overall Removal (%)	99
k_v (min^{-1})	<0.001
k_b, Calculated (min^{-1})	0.01
Q_a (liters/min)	4.0
MLSS (mg/l)	3260

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING k_b MEASURED IN CMB STUDY

Effluent (μg/ℓ)	46
Off-Gas (ng/ℓ)	353
N/N_o	0.04
Overall Removal (%)	96

TABLE 10-46

SUMMARY OF RESULTS FROM AERATED CMB BIODEGRADATION RATE STUDIES

Compound	k_o (min^{-1})	Q_a (ℓ/min)	k_v (min^{-1})	k_b (min^{-1})	Overall Removal (%) Measured	Overall Removal (%) Predicted
Benzene	0.179	4.3	0.079	0.10	65	55
	0.436	4.0	0.074	0.36	75	82
	0.471	4.1	0.076	0.39	81	84
	0.582	4.5	0.084	0.50	88	87
Toluene	0.434	4.2	0.081	0.35	84	81
Chlorobenzene	0.333	4.3	0.053	0.28	87	86
	0.484	4.3	0.053	0.43	83	90
Nitrobenzene	0.09	4.2	<0.001	0.09	98	96
	0.08	4.0	<0.001	0.08	99	96

10.5.3. Conclusions

Results from the two types of biodegradation rate studies provided conclusive evidence that the disappearance of the toxic organic compounds observed in the CMF activated sludge studies was a result of biodegradation by activated sludge microorganisms. Batch degradation studies demonstrated biodegradation of benzene, toluene, ethylbenzene, chlorobenzene, and nitrobenzene occurred at the microgram-per-liter concentration range typical of municipal wastewaters. Although biodegradation rate studies were not conducted with o-xylene or 1,2-dichlorobenzene, similar findings would be expected for these compounds.

The results from non-aerated biodegradation rate studies demonstrated that the biodegradation of microgram-per-liter concentrations of the test compounds could be successfully described by a first-order model. In general biodegradation rate coefficients measured in batch rate studies were in good agreement with values calculated from a CMF bioreactor mass balance approach. Aerated biodegradation rate studies conducted in 10-liter bioreactors operated in batch modes, indicated that the overall reduction in aqueous concentration (volatilization plus biodegradation) could be described by a first-order model, also. This finding provided support for the hypothesis that independently measured first-order removal coefficients for volatilization, k_v, and biodegradation, k_b, could be combined to give an overall first-order removal rate coefficient, k_o. Measured steady-state biodegradation rate coefficients of the highly biodegradable (overall removals > 75%), volatile compounds were significantly larger than their corresponding volatilization rate coefficients for the operating conditions used in the CMF bioreactors. This result was indicated by the mass balance approach, Equation 10-4, used to estimate biodegradation rate coefficients from influent, effluent and off-gas analyses. Ratios of k_b/k_v for steady-state biodegradation of the volatile compounds generally were in the 5.0 to 6.0 range. The ratios k_b/k_o for the compounds examined in the batch biodegradation studies were approximately the same as the fraction of the mass fluxes of biodegradable compounds into the CMF bioreactors that were removed by biodegradation. In general the ratio of k_b/k_o ranged from 0.75 to 0.85.

Equation 10-9 can be rearranged and written to describe the fate of the toxic organic compounds in CMF reactors using three pieces of information: independently measured volatilization and biodegradation rate coefficients and the mean hydraulic retention time

$$\frac{k_b}{k_b + k_v + 1/\bar{t}} = 1 - \frac{N}{N_o} \qquad (10\text{-}14)$$

The left-hand side of the equation, $k_b(k_b + k_v + 1/\bar{t})^{-1}$ represents the fraction of the influent removed by biodegradation. The fraction of the influent leaving the CMF bioreactors in effluents and off-gas can be described by

$$\frac{k_v + 1/\bar{t}}{k_b + k_v + 1/\bar{t}} = \frac{N}{N_o} \qquad (10\text{-}15)$$

The following three equations can be used to model the fate of the toxic organic compounds in the CMF bioreactors

$$\text{fraction of influent biodegraded, } f_b = \frac{k_b}{k_b + k_v + 1/\bar{t}} \qquad (10\text{-}16)$$

$$\text{fraction of influent volatilized, } f_v = \frac{k_v}{k_b + k_v + 1/\bar{t}} \qquad (10\text{-}17)$$

$$\text{fraction of influent in effluent, } f_e = \frac{1/\bar{t}}{k_b + k_v + 1/\bar{t}} \qquad (10\text{-}18)$$

The examples calculated in Table 10-47 for benzene, chlorobenzene, 1,2,4-trichlorobenzene and nitrobenzene illustrate how independently determined values of k_b and k_v can be used to estimate the fate of each compound in the experimental system without considering aqueous or gas phase concentrations. Values for k_b for biodegradable compounds used in the illustration were measured in the batch biodegradation experiments. The value of k_b for non-biodegradable compounds was assumed to be zero. The hydraulic retention time, $\bar{t}$, used in the calculations was 5.5 hours. The fractions of the influents predicted to be biodegraded, volatilized and discharged in effluents by Equations 10-16, 10-17, and 10-18 were approximately the same as observed in the activated sludge bioreactor studies. Values of k_v were calculated using Equation 7-2 and the volatilization parameters measured in the batch volatilization studies.

10.6 MULTI-SOLUTE STUDY

The results presented thus far were obtained from activated sludge bioreactor studies in which only one compound was added to the influent of a given unit. Influents to full scale activated sludge facilities typically have been reported to contain a wide variety of toxic organic compounds rather than a single toxic compound (4,5,6). A multi-solute study was designed to evaluate the removal of seven toxic organics added simultaneously to the influent of an activated sludge bioreactor. The removal of each compound had been well characterized in single solute activated sludge bioreactors. Five of the seven compounds, benzene,

TABLE 10-47

FATE OF THREE COMPOUNDS CALCULATED WITH EQUATIONS 10-16 THROUGH 10-18
USING INDEPENDENTLY MEASURED RATE PARAMETERS k_b and k_v

Compound	k_b (min^{-1})	k_v (min^{-1})	$1/\bar{t}$ (min^{-1})	Biodegraded $\frac{k_b}{k_b+k_v+1/\bar{t}}$	Volatilized $\frac{k_v}{k_b+k_v+1/\bar{t}}$	Effluent $\frac{1/\bar{t}}{k_b+k_v+1/\bar{t}}$
Benzene	0.27	0.074	0.003	0.78	0.21	0.01
	0.57	0.074	0.003	0.88	0.11	<0.01
Chlorobenzene	0.22	0.050	0.003	0.81	0.18	0.01
Nitrobenzene	0.09	<0.001	0.003	0.96	<0.01	0.04
1,2,4-Trichlorobenzene	0	0.025	0.003	0	0.89	0.11

Q_a = 4.0 ℓ/min

toluene, chlorobenzene, ethylbenzene, and o-xylene were observed to be readily biodegradable while the remaining two compounds, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, were found to be poorly degraded and non-biodegradable, respectively.

The multi-solute activated sludge unit was operated under steady-state conditions with respect to influent TOC, solids retention time and hydraulic retention time. A summary of pertinent bioreactor operating conditions is given in Table 10-48.

The bioreactor was initially seeded with activated sludge from the secondary aeration basin of the Ann Arbor Wastewater Treatment facility. Approximately twenty days were provided to acclimate the activated sludge to the synthetic wastewater before the toxic organic compounds were added to the influent. The multi-solute study was conducted for a total of 100 days which can be divided into five different periods, summarized in Table 10-49, based on the influent concentrations of the toxic compounds.

TABLE 10-48

BIOREACTOR OPERATING CONDITIONS FOR
THE MULTI-SOLUTE ACTIVATED SLUDGE STUDY

Toxic Organic Solutes: Benzene, Toluene, Ethylbenzene, o-xylene, Chlorobenzene, 1,2-Dichlorobenzene, and 1,2,4-Trichlorobenzene

Solids Retention Time: 6 days

Hydraulic Retention Time: 5.5 hours

Avg. Influent TOC: 112 mg/ℓ

Avg. TOC Removal: 84.6%

Avg. MLSS: 3700 mg/ℓ

Aeration Rate: 3.8-4.4 ℓ/min (Avg = 4.1)

TABLE 10-49

MULTI-SOLUTE BIOREACTOR OPERATING PERIODS WITH RESPECT TO THE CONCENTRATIONS OF THE TOXIC SOLUTES

Time Period	Length (days)	Operating Conditions
1. Days 0-45	45	Steady-state Influent conc. of all toxic organic compounds between 100 and 150 μg/ℓ
2. Days 46-62	17	Spike loadings of benzene, ethylbenzene, and chlorobenzene
3. Days 63-76	14	No toxics added to influent
4. Days 77-83	7	Spike loadings of benzene, ethylbenzene, and chlorobenzene producing influent concentrations between 8,000 and 12,000 μg/ℓ
5. Days 84-100	17	Steady-state influent conc. of all toxics between 100 and 200 μg/ℓ

An important objective of the multi-solute study was to compare the removal of each toxic solute to results obtained from single solute studies in which only one compound had been added to the influent of a bioreactor. During the first 45 days of the multi-solute study the bioreactor was operated with influent concentrations of each compound in the 100 to 150 μg/ℓ range. Influent, effluent and off-gas samples were collected every three to four days for the five biodegradable compounds, benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene and every four to six days for 1,2-dichlorobenzene and 1,2,4-trichlorobenzene.

Influent, effluent, and off-gas concentrations and N/N_o values for each compound during the first 45 days of the multi-solute study were plotted in Figures 10-87 through 10-91 with results from single solute studies conducted under identical operating conditions. The similarities of the N/N_o curves in Figures 10-87 through 10-91 indicated that there was no significant difference in the behavior of each compound in single and multi-solute systems. Each biodegradable compound experienced a 14 to 21 day acclimation phase followed by a period of relatively steady-state removal due to biodegradation. A comparison of acclimation periods and overall removals from single and multi-solute studies is given in Table 10-50.

Results from single solute studies produced the following order of biodegradative removal of the five biodegradable compounds, benzene ≈ toluene > chlorobenzene > ethylbenzene > o-xylene. Similar findings were obtained from the multi-solute study as shown in Figures 10-92 and 10-93 and Table 10-51.

A distinctive feature of the multi-solute results was the sudden increase in fractional recoveries of the biodegradable compounds on Day 35 as shown by the increase in N/N_o values in Figures 10-87 through 10-91. This period corresponded to a decrease in mixed liquor pH from 7.2 to 6.4 due to a problem with the pump delivering the portion of the influent to the bioreactor containing $NaHCO_3$. The pH was adjusted to its steady-state level of between 7.1 and 7.3 within 12 to 18 hours, and the bioreactor samples collected on Day 37 indicated that the overall removal of each compound except o-xylene had returned to its steady-state level within 48 hours. During the pH-induced upset period the recoveries of ethylbenzene and o-xylene approached the 90% level indicating very little biodegradation was occurring. Recoveries of benzene and toluene increased to approximately 70% while chlorobenzene was least affected with a recovery of 60% recorded on Day 35. Table 10-51 provides a comparison of overall removals measured under steady-state conditions and on Day 35 after the approximate 0.8 unit decrease in the mixed liquor pH.

Influent concentrations of benzene, ethylbenzene, and chlorobenzene to the multi-solute bioreactor were increased from approximately 100 to 1000 μg/ℓ on Day 48. Concurrently, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene were omitted from the influent. Influent, effluent, and off-gas concentrations and N/N_o values measured between Days 0 and 64 for each compound are given in Figures 10-94 through 10-98.

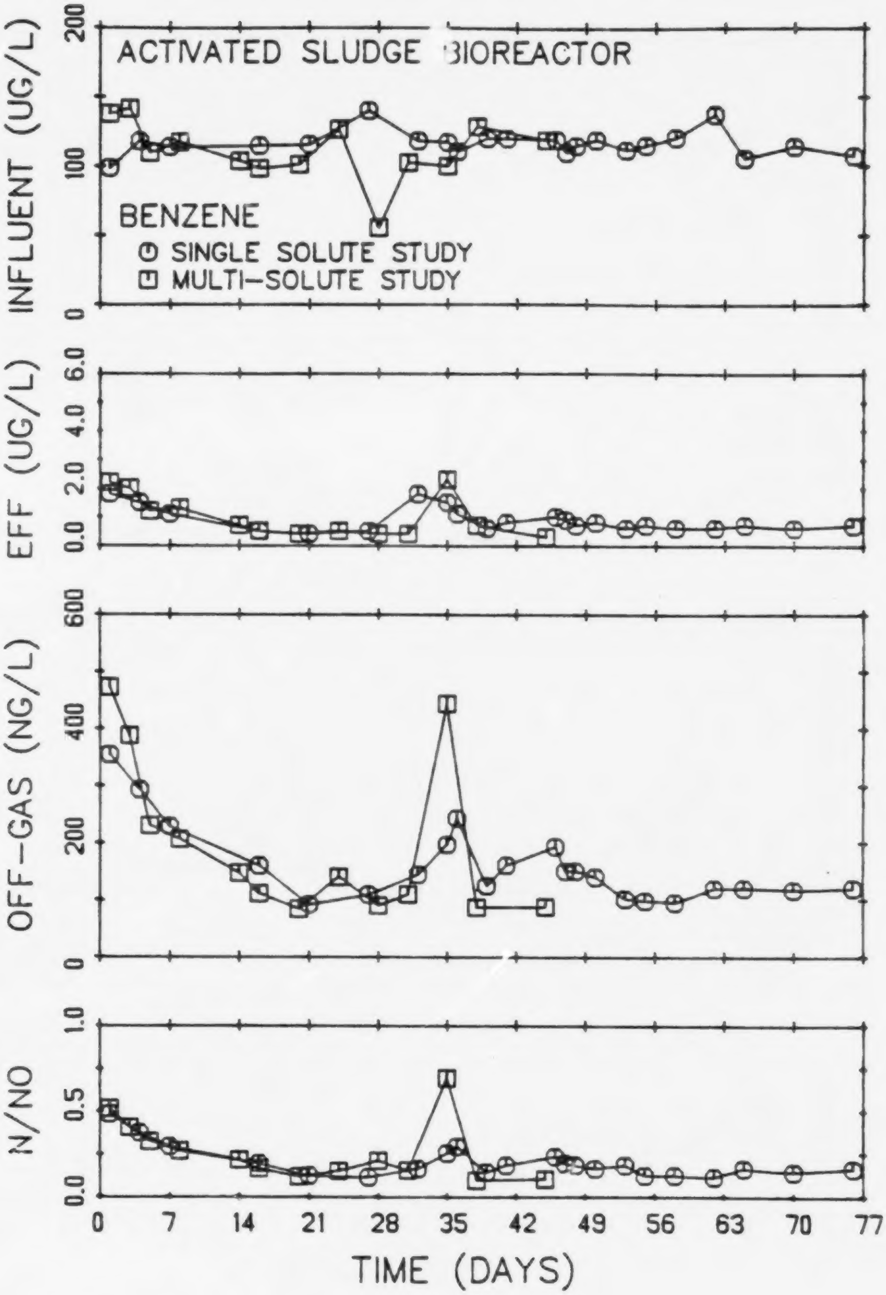


FIGURE 10-87. Comparison of benzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during single solute and multi-solute activated sludge studies.

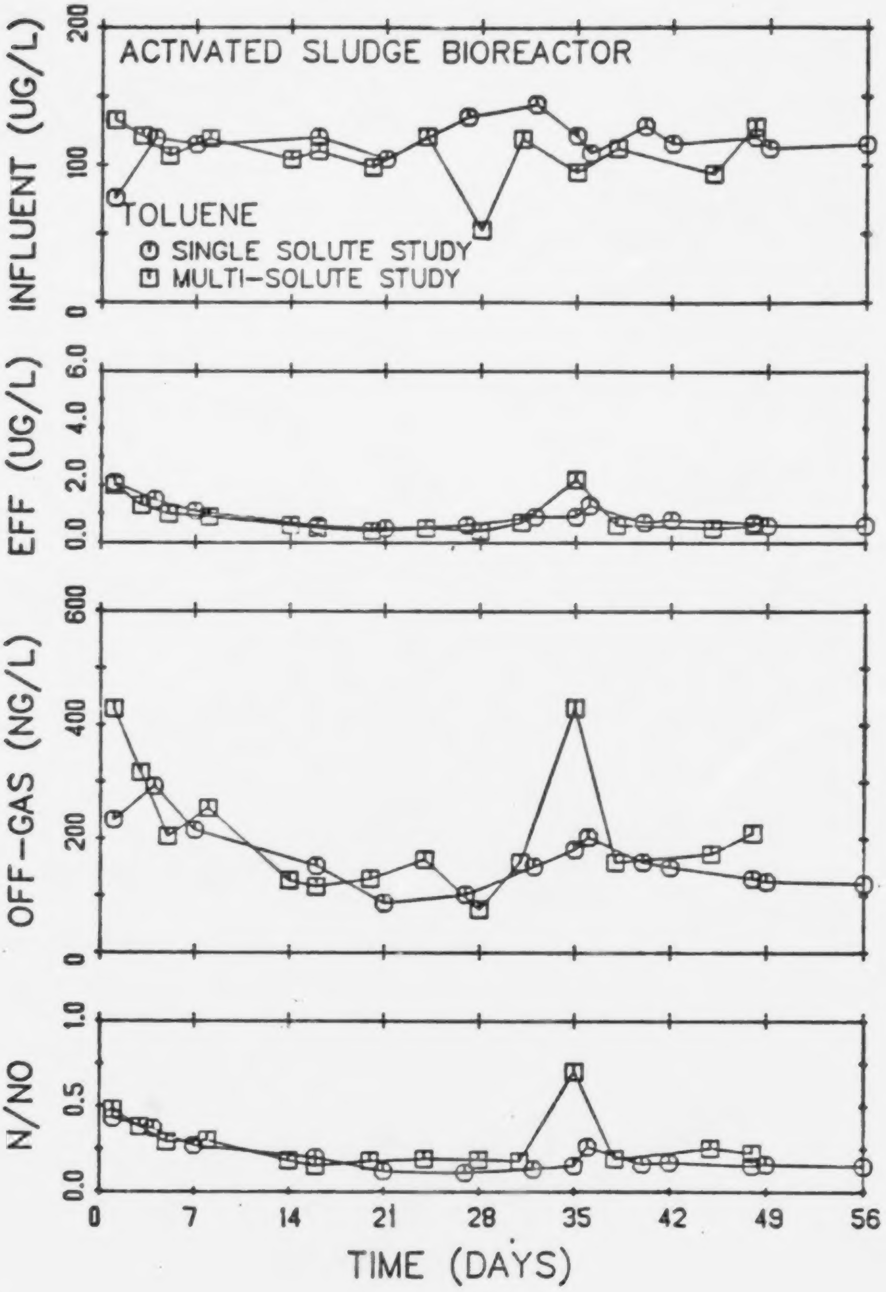


FIGURE 10-88. Comparison of toluene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during single solute and multi-solute activated sludge studies.

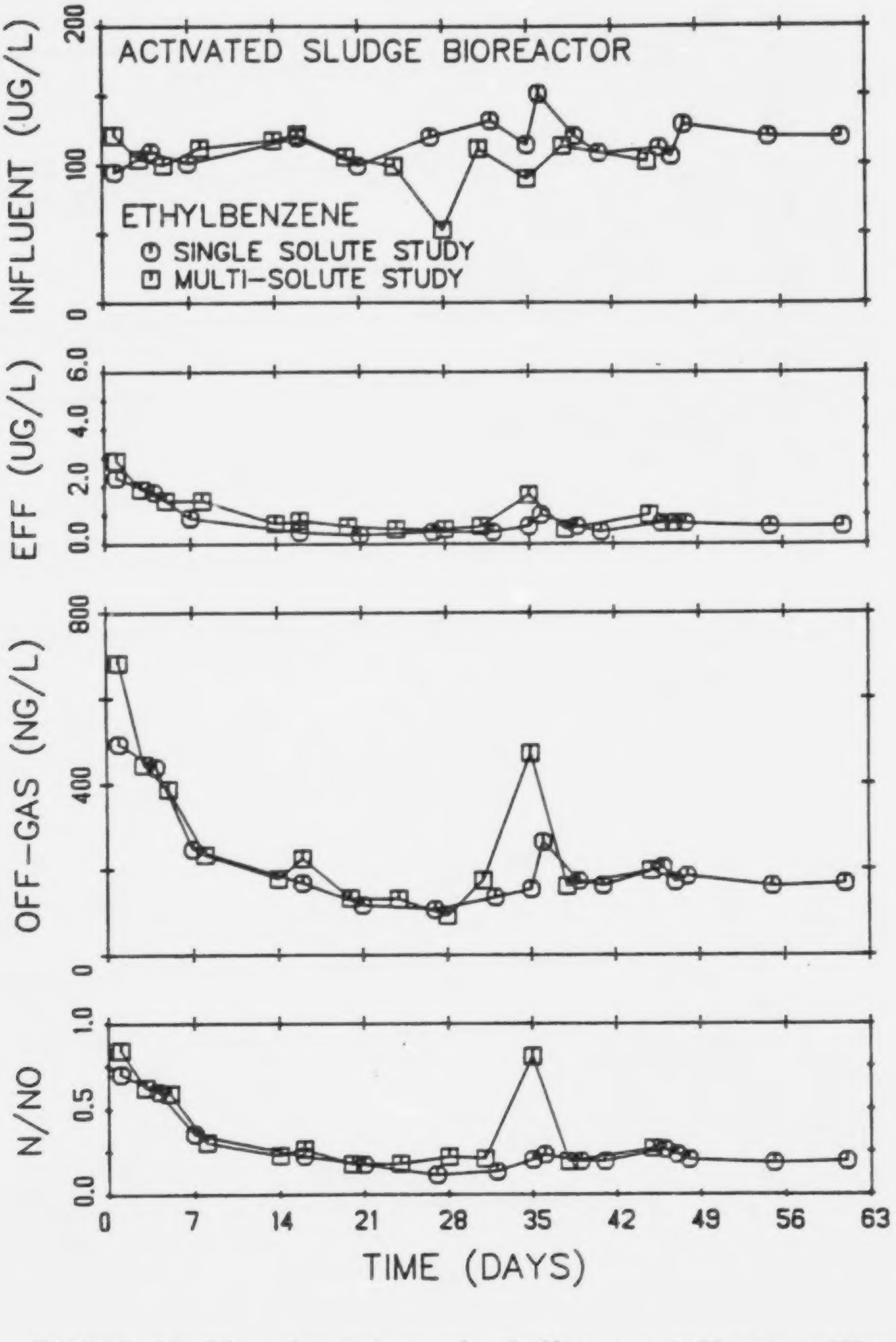


FIGURE 10-89. Comparison of ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during single solute and multi-solute activated sludge studies.

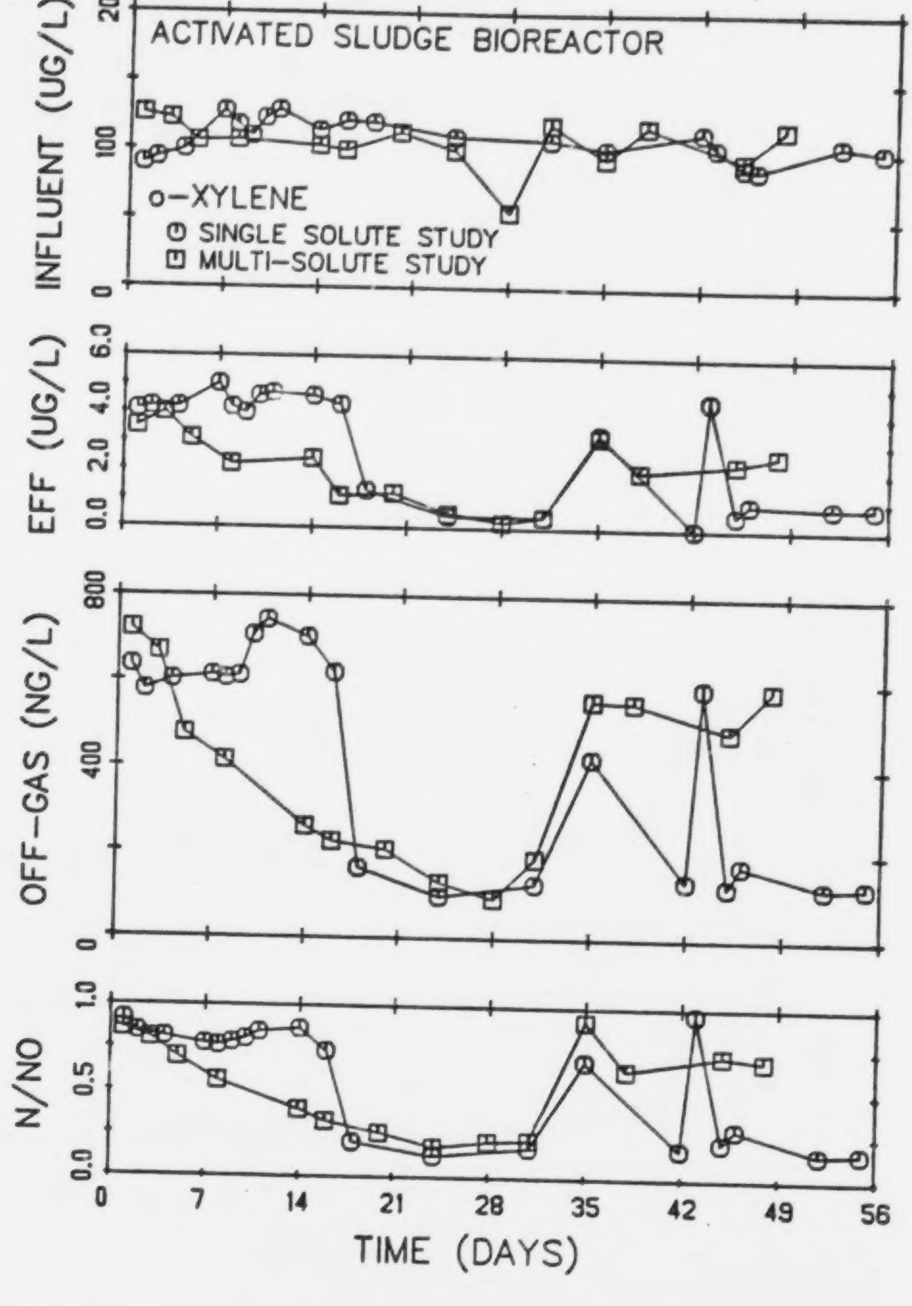


FIGURE 10-90. Comparison of o-xylene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during single solute and multi-solute activated sludge studies.

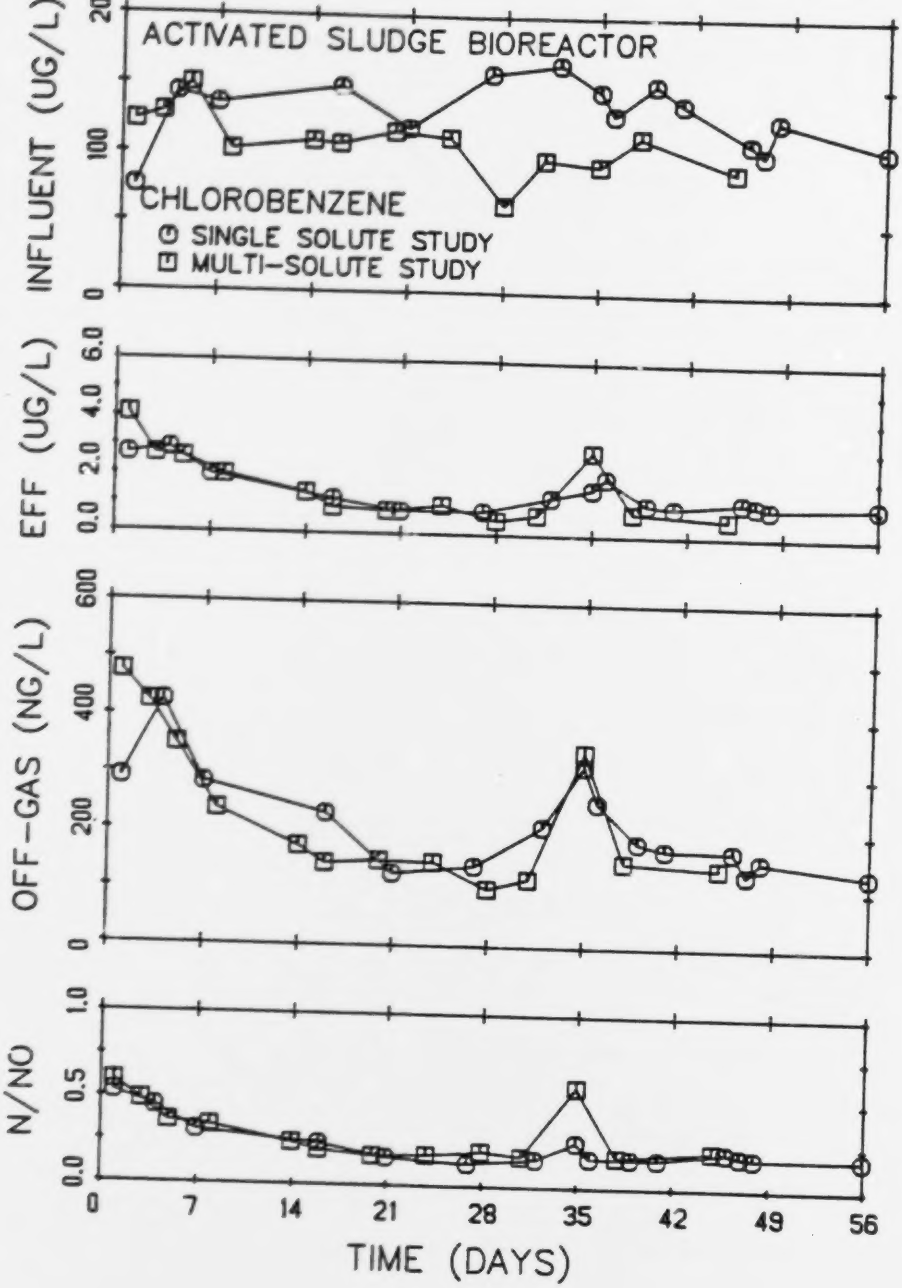


FIGURE 10-91. Comparison of chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during single solute and multi-solute activated sludge studies.

TABLE 10-50

COMPARISON OF ACCLIMATION PERIODS AND STEADY STATE TOXICS REMOVALS FROM SINGLE SOLUTE AND MULTI-SOLUTE ACTIVATED SLUDGE STUDIES

	Acclimation Period (days)		Overall Removal (%)	
Compound	Single Solute	Multi Solute	Single Solute+	Multi Solute++
Benzene	14-21	14-21	84 (5)	86 (4)
Toluene	14-21	14-21	84 (4)	81 (3)
Ethylbenzene	14-21	14-21	80 (4)	79 (4)
o-Xylene	14-21	21-24	78 (4)	78 (3)+++
Chlorobenzene	14-21	14-21	82 (3)	81 (2)
1,2-Dichlorobenzene	14-21	14-21	37 (6)	41 (12)
1,2,4-Trichlorobenzene	0	0	0	0

( ) Standard Deviation

+ Average of all activated sludge studies for that compound conducted at a 6-day SRT

++ Day 20 through Day 46, excluding Day 35

+++ Includes Day 20 through Day 31 only

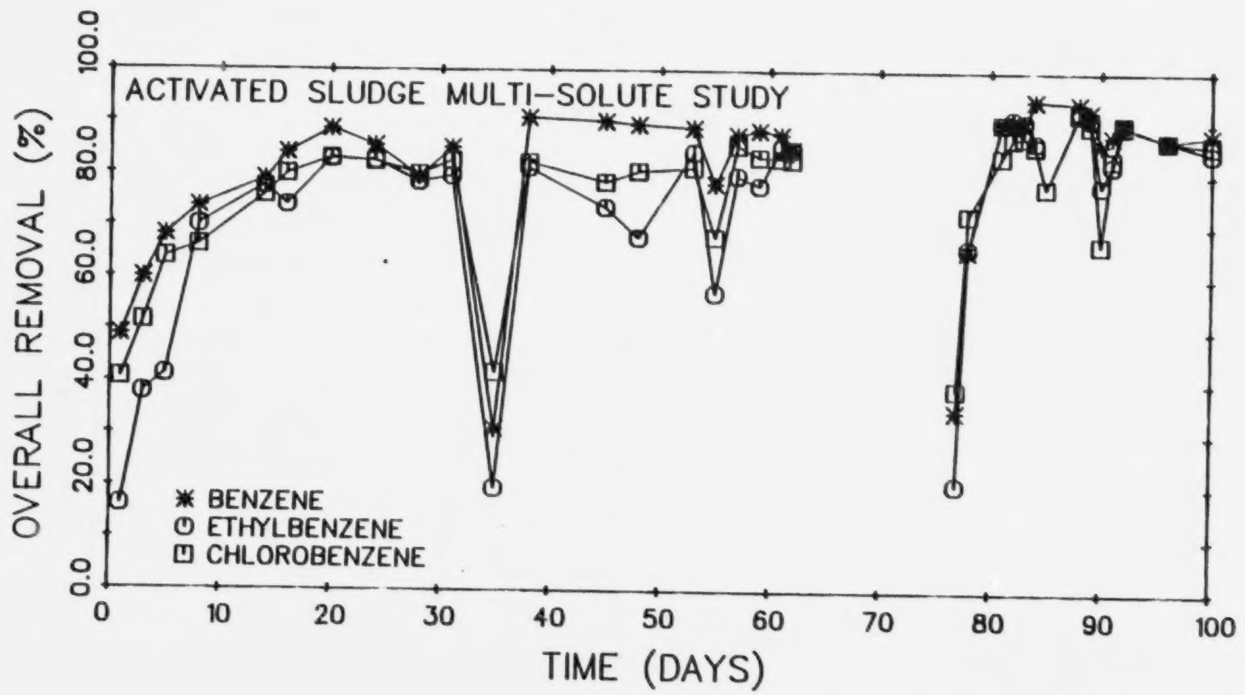


FIGURE 10-92. Comparison of benzene, ethylbenzene, and chlorobenzene overall removals due to biodegradation measured during the multi-solute activated sludge study.

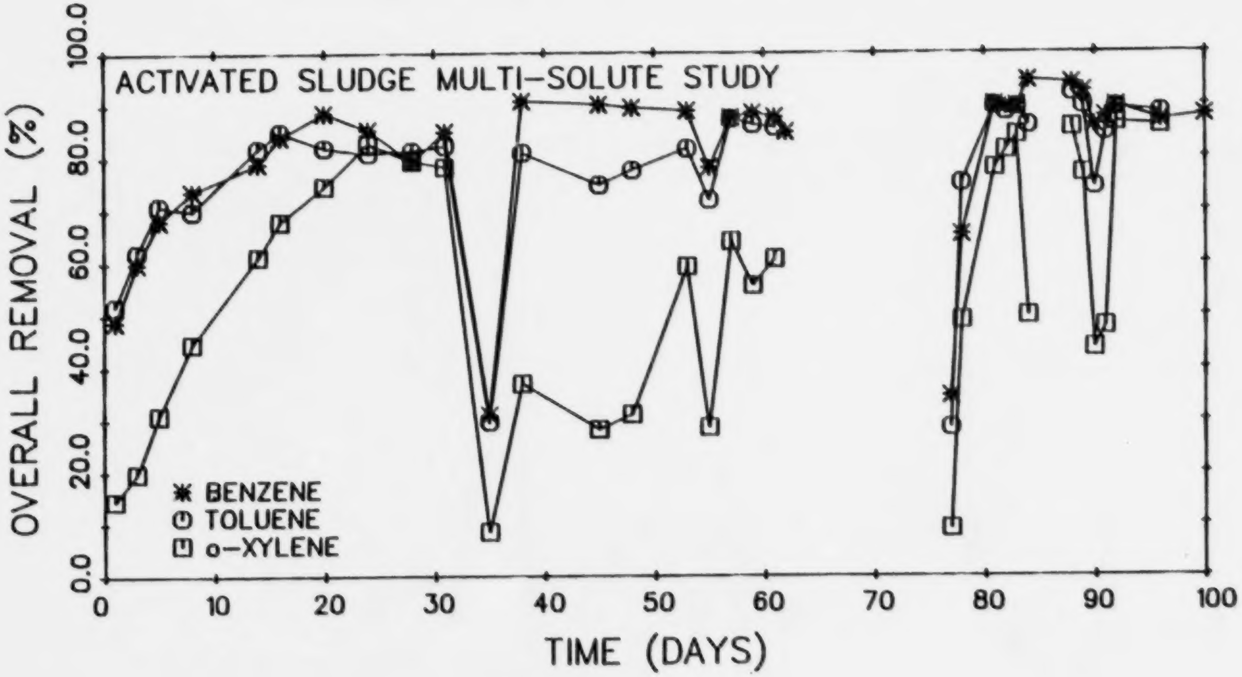


FIGURE 10-93. Comparison of benzene, toluene, and o-xylene overall removals due to biodegradation measured during the multi-solute activated sludge study.

TABLE 10-51

EFFECT OF pH-INDUCED UPSET ON BIODEGRADATION RATE COEFFICIENTS AND OVERALL REMOVALS OF BIODEGRADABLE COMPOUNDS

Compound	Overall Removal (%) Steady-state[1]	Overall Removal (%) Day 35	Biodegradation Rate Coeff (min^{-1}) Steady-state[1]	Biodegradation Rate Coeff (min^{-1}) Day 35
Benzene	86	31	0.472	0.035
Toluene	81	30	0.340	0.034
Ethylbenzene	79	20	0.322	0.022
o-Xylene	78*	<10	0.215	0.006
Chlorobenzene	81	42	0.219	0.038

[1] Mean value averaged from data collected between Days 20 and 45 omitting Day 35.

* Data from Day 20 to Day 31 only.

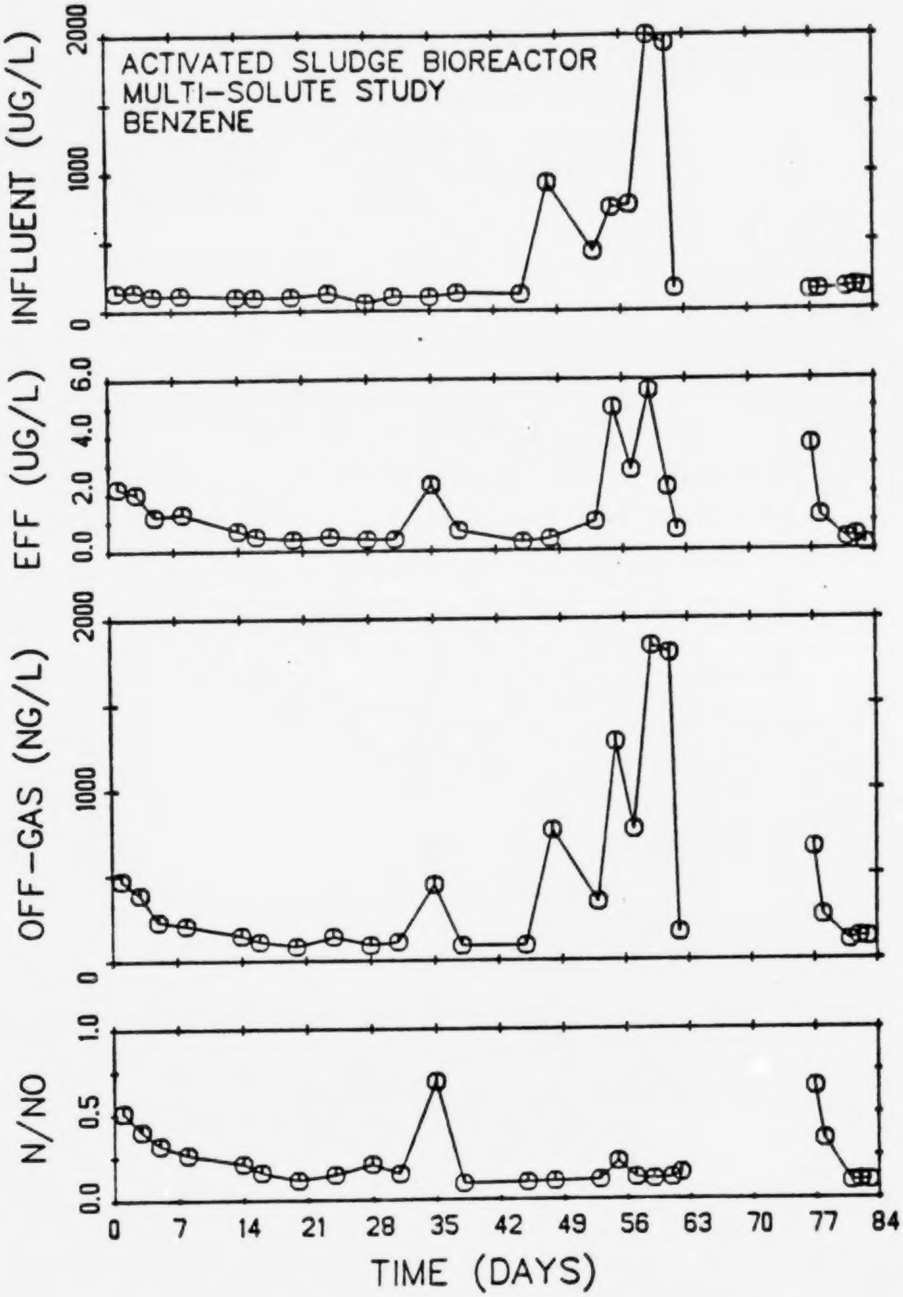


FIGURE 10-94. Effect of an increase in influent toxics concentrations and an interruption in toxics addition to the bioreactor on benzene effluent and off-gas concentrations and fractional recoveries, N/No, during the multi-solute study.

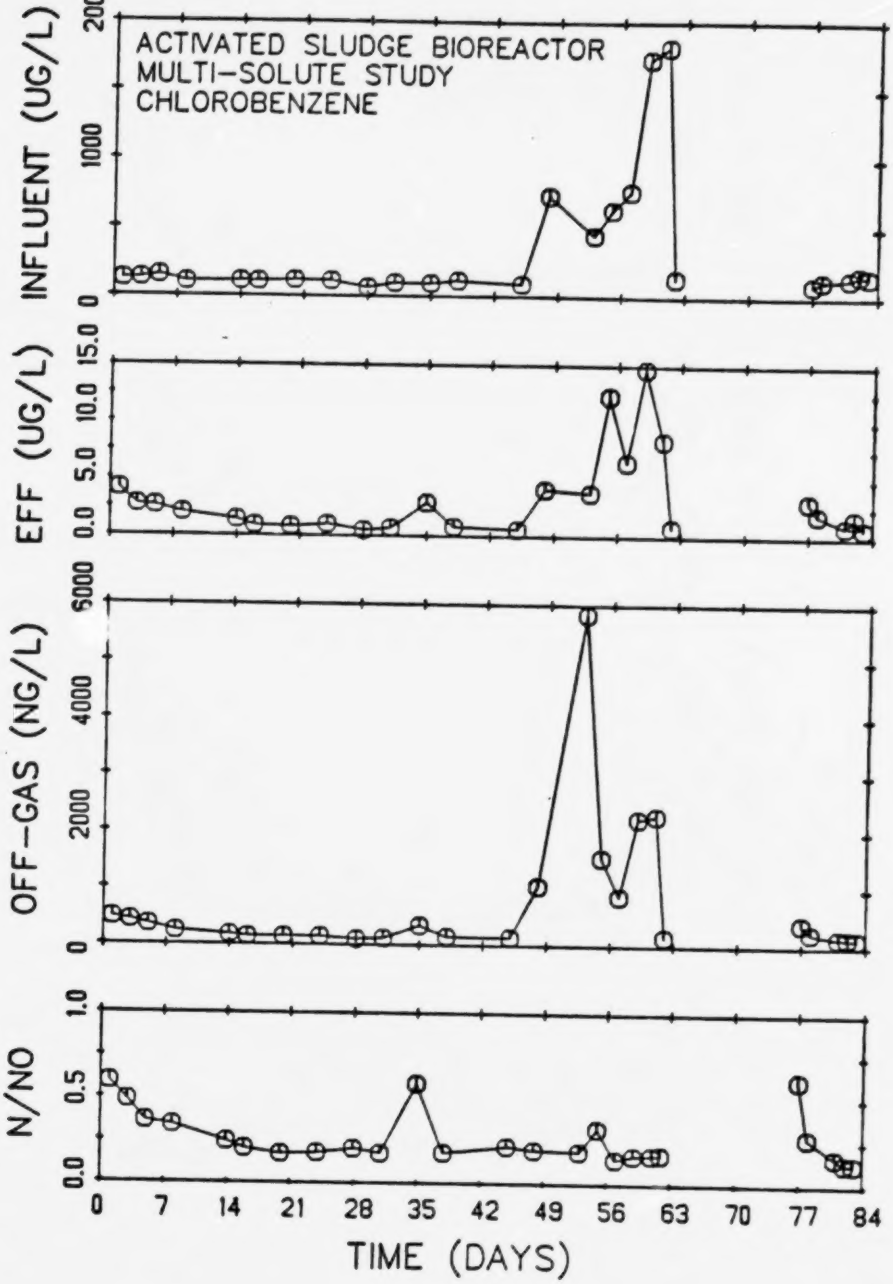


FIGURE 10-95. Effect of an increase in influent toxics concentrations and an interruption in toxics addition to the multi-solute activated sludge bioreactor on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

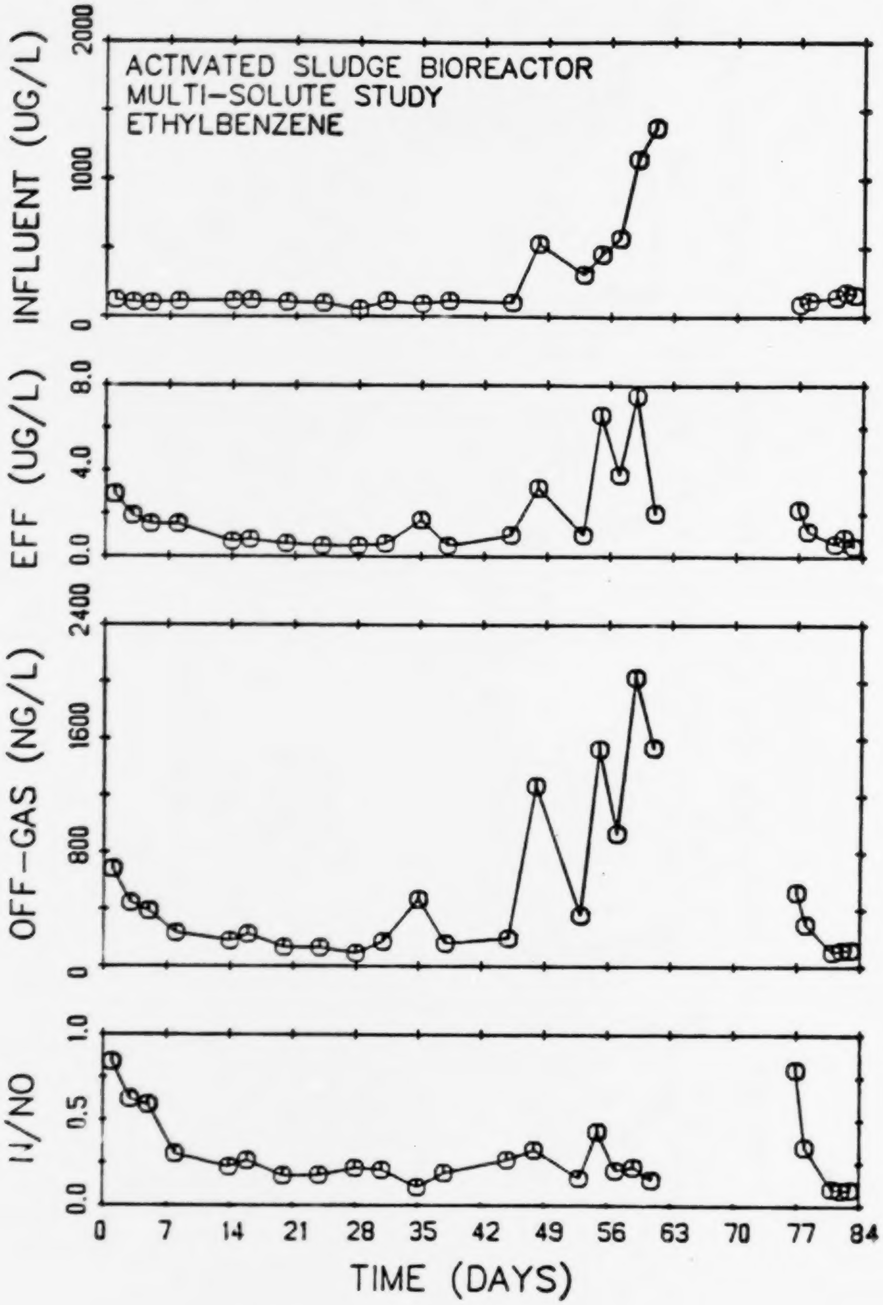


FIGURE 10-96. Effect of an increase in influent toxics concentrations and an interruption in toxics addition to the multi-solute activated sludge bioreactor on ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No.

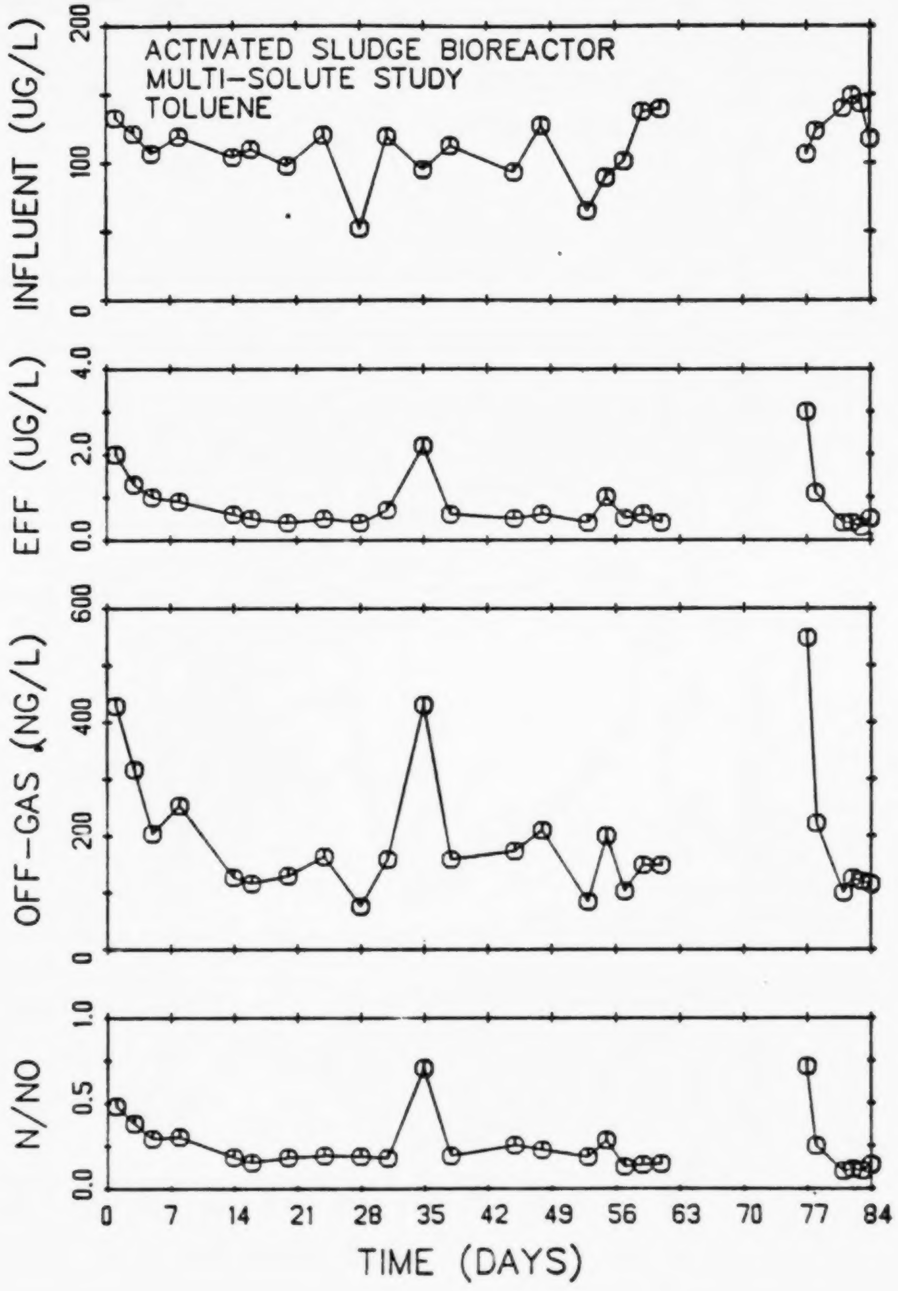


FIGURE 10-97. Effect of an increase in influent toxics concentrations and an interruption in toxics addition to the multi-solute activated sludge bioreactor on toluene effluent and off-gas concentrations and fractional recoveries, N/No.

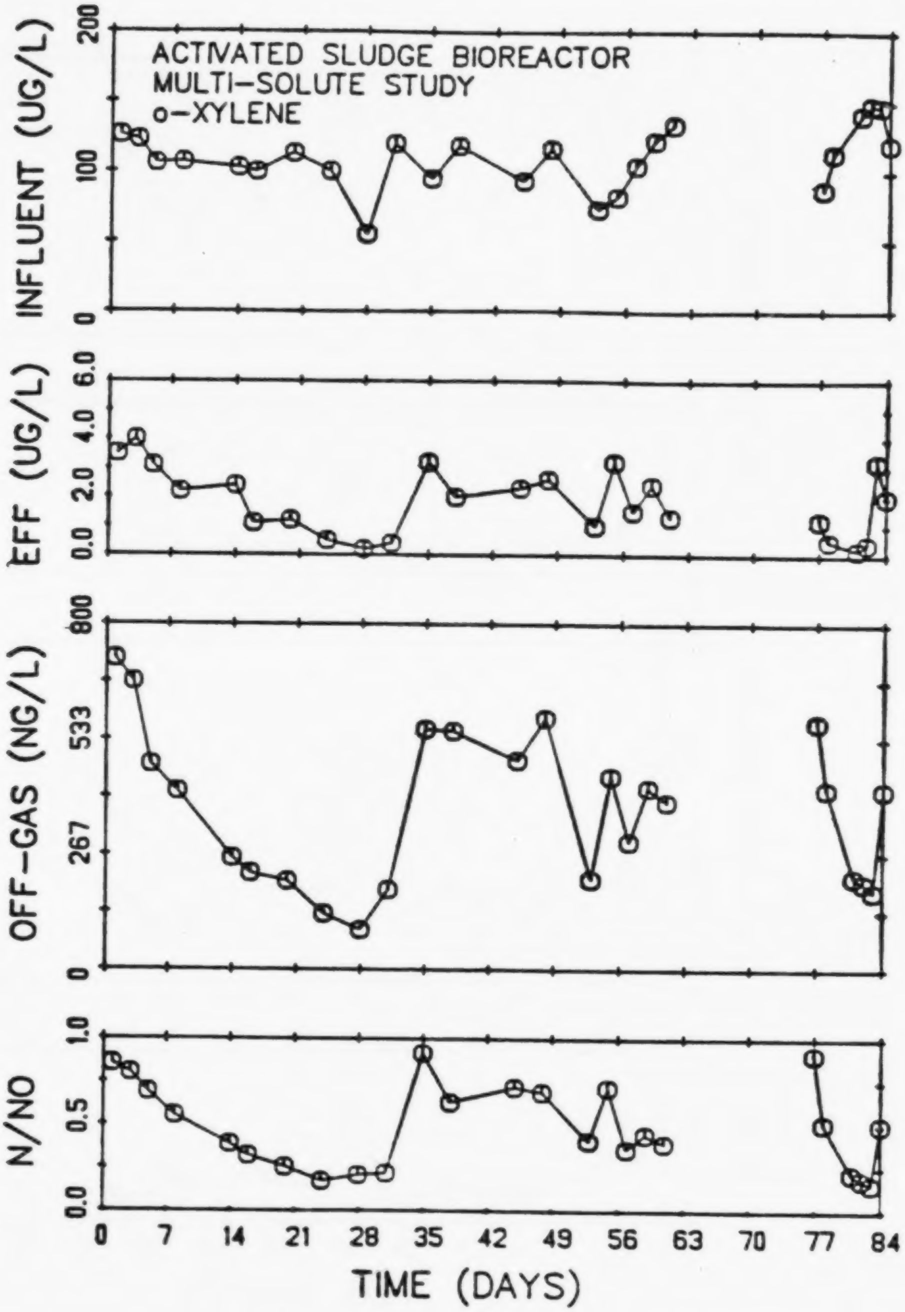


FIGURE 10-98. Effect of an increase in influent toxics concentrations and an interruption in toxics addition to the multi-solute activated sludge biorector on o-xylene effluent and off-gas concentrations and fractional recoveries, N/No.

The overall removal of benzene was not affected by the spike loadings of benzene, ethylbenzene, and chlorobenzene as indicated by the relative constant N/N_0 values in Figure 10-94 between Days 49 and 63. With the exception of the sample collected on Day 55, the overall removal of benzene exceeded 85% during this period. The mean benzene removal during the period of high influent concentrations was 86.5% compared to 86.2% during the preceding four weeks when the influent was in the 100-150 μg/ℓ range. The effluent concentration reached a maximum value of only 5.8 μg/ℓ even though the influent concentration was increased to approximately 2000 μg/ℓ. If biodegradation of benzene had not occurred the effluent concentration resulting from a 2000 μg/ℓ influent concentration would have been approximately 80 μg/ℓ, according to the air-stripping model previously developed.

The results for chlorobenzene presented in Figure 10-95 indicated that, like benzene, the overall removal did not change as a result of the increased influent concentrations of benzene, ethylbenzene, and chlorobenzene. A mean overall chlorobenzene removal of 80.6% was recorded during the period of high influent concentrations compared to 81.4% during the preceding steady-state toxics removal period characterized by influent concentrations ranging from 100 to 150 μg/ℓ. The increased chlorobenzene concentration from 90 to approximately 730 μg/ℓ on Day 48 produced an increase in the effluent concentration from the steady-state level of 0.8 to only 4.1 μg/ℓ.

Further increases in the influent chlorobenzene concentration to 1800 μg/ℓ caused the effluent to increase to 14.7 μg/ℓ. In the absence of chlorobenzene biodegradation the effluent concentration would have increased to over 100 μg/ℓ between Days 56 and 63.

The results presented in Figure 10-96 for ethylbenzene show that the effluent concentration remained less than 8 μg/ℓ even though the influent concentration reached approximately 1300 μg/ℓ. Overall ethylbenzene removal due to biodegradation averaged 79.7% during the operating period with steady-state influent concentrations between 100 and 150 μg/ℓ, compared with 75.3% during the period with increased influent concentrations. As also observed during the first 45 days, ethylbenzene removal due to biodegradation was less than either benzene or chlorobenzene under conditions of elevated influent concentrations.

The influent concentrations of toluene and o-xylene were not increased on Day 48. Toluene averaged 106 μg/ℓ in the influent during the period of increased benzene, ethylbenzene, and chlorobenzene influent concentrations, Days 48 to 63. The increased influent concentrations of benzene, ethylbenzene, and chlorobenzene caused no measurable variation in the biodegradation of toluene. Overall removals averaged 81.2 and 81.8% between Days 0 to 47 and Days 48 to 63, respectively. As shown by Figure 10-97 effluent and off-gas concentrations exhibited only small fluctuations during the initial nine weeks of the study once steady-state toluene biodegradation had been attained.

The overall removal of o-xylene was considerably less than the other four compounds throughout the first nine weeks. The results presented in Figure 10-98 show that unlike benzene, toluene, ethylbenzene or chlorobenzene, the overall removal of o-xylene did not return to its previous level after the pH-induced upset on Day 35. Instead, overall o-xylene removal averaged only 32.1% during the ten days following the upset compared with 78.8% measured during the eleven days preceding the upset. After the influent concentrations of benzene, ethylbenzene, and chlorobenzene were increased on Day 48 the removal of o-xylene increased to approximately 60% where it remained through Day 62. While the results were inconclusive whether or not the increased influent concentrations of benzene, ethylbenzene and chlorobenzene affected the degradation of o-xylene two points suggest that they did not. First, activated sludge microorganisms were exposed to at most 15 μg/ℓ of any one compound, since the effluent concentration was the concentration in the aeration basin of the CMF bioreactor. Such low levels likely did not inhibit o-xylene biodegradation.
Secondly, biodegradation of o-xylene actually improved after Day 48 when the influent concentrations of benzene, ethylbenzene, and chlorobenzene were increased. During the operating period between the pH-induced upset on Day 35 and Day 48, overall o-xylene removal remained at a depressed level of only 32%. Influent concentrations of all toxic organic compounds were in the 100 to 150 μg/ℓ range during this time.

No toxic organic compounds were added to the influent of the multi-solute bioreactor for a period of 14 days between Days 63 and 76. This was done to determine if the activated sludge experienced another acclimation phase or if the microorganisms retained their ability to degrade the toxic organic compounds during the two week period of non-exposure to them. When the toxics were again added to the influent, the influent concentration of each of the five biodegradable compounds was approximately 150 μg/ℓ. Each compound experienced a reacclimation phase as shown by Figures 10-94 to 10-98 and by Figures 10-99 through 10-103 in which the initial acclimation and reacclimation periods have been compared. Day 0 of the reacclimation period in Figures 10-99 through 10-103 represents the reintroduction of toxics to the influent of the multi-solute reactor on Day 77.

The reacclimation period was characterized by a rapid return of effluent, off-gas and N/N_0 values to steady-state levels. Within three to four days overall removals of benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene increased to the same steady-state levels observed after the initial two to three week acclimation period as shown by the comparisons in Table 10-52.

Influent concentrations of the toxic compounds were increased a second time during the final two weeks of the multi-solute study. Maximum concentrations of benzene, ethylbenzene and chlorobenzene were between 8000 and 12000 μg/ℓ while maximum toluene and o-xylene concentrations were an order of magnitude lower. Also added to the influent at concentrations ranging from 200 to 2000 μg/ℓ were

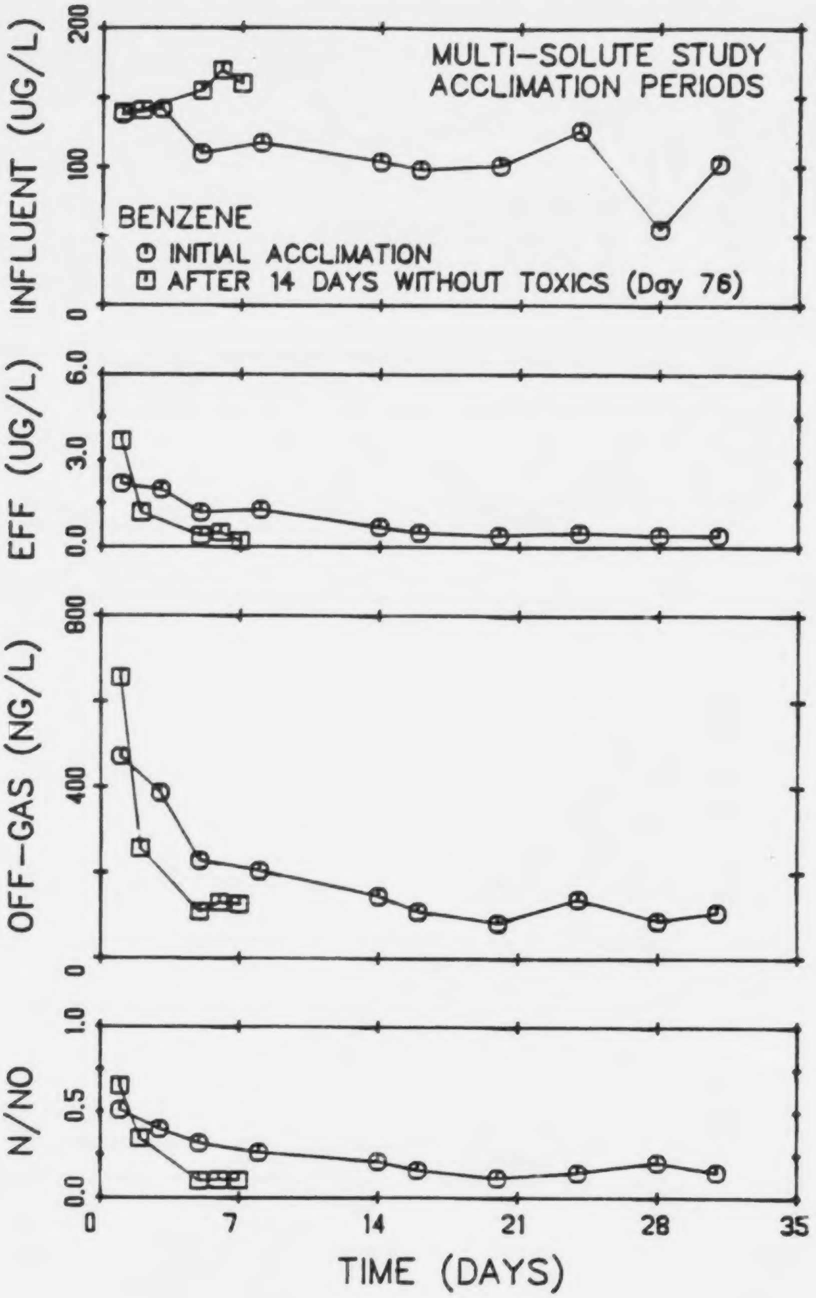


FIGURE 10-99. Initial activated sludge acclimation to benzene and reacclimation after a 14-day interruption in toxics addition to the influent during the multi-solute activated sludge study.

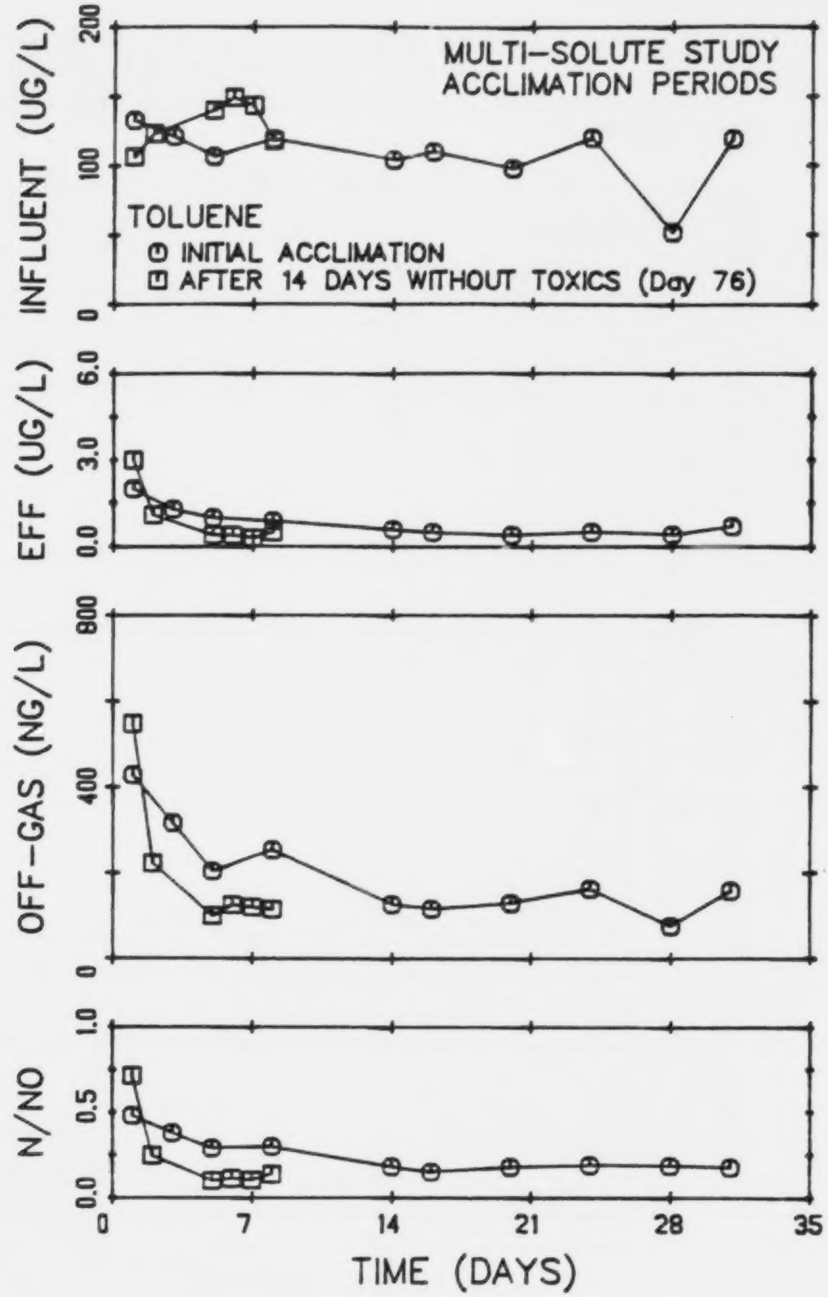


FIGURE 10-100. Initial activated sludge acclimation to toluene and reacclimation after a 14-day interruption in toxics addition to the influent during the multi-solute activated sludge study.

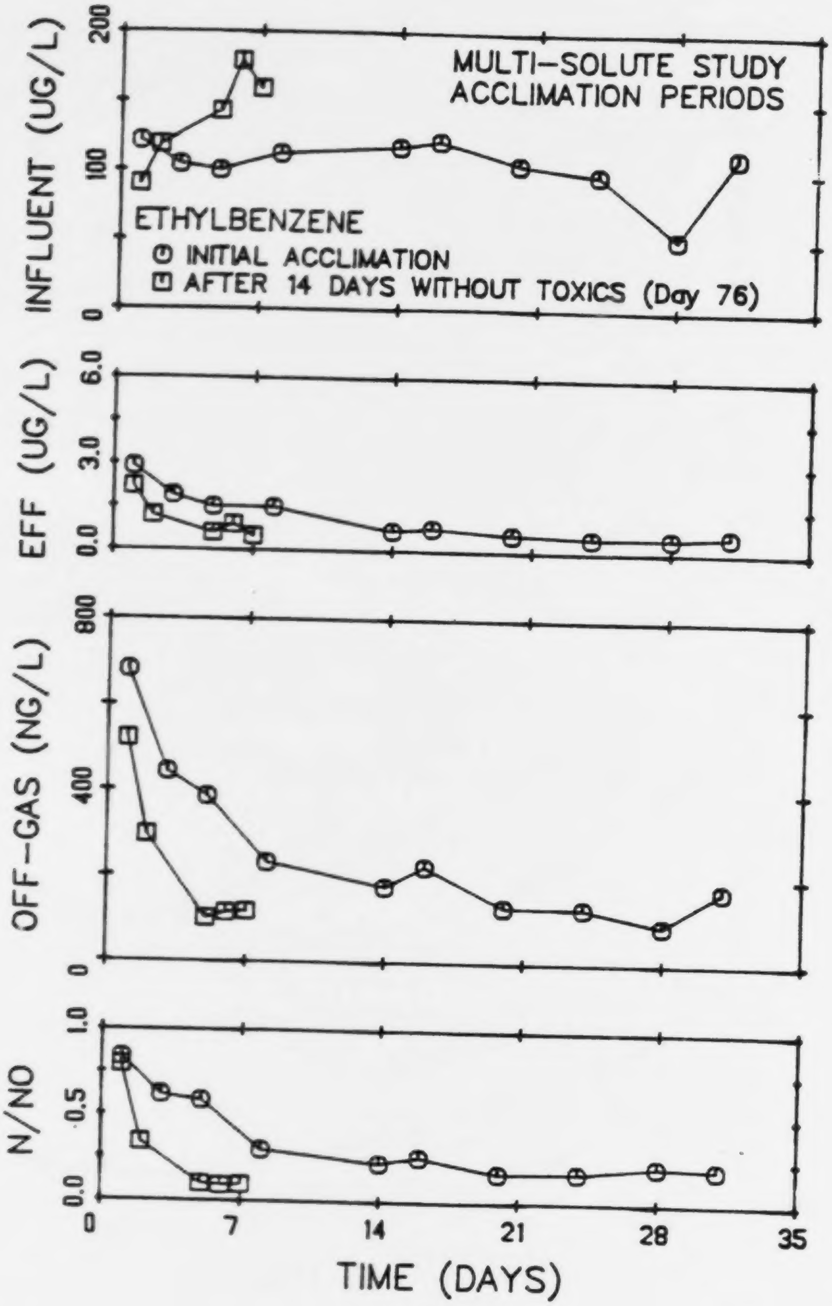


FIGURE 10-101. Initial activated sludge acclimation to ethylbenzene and reacclimation after a 14-day interruption in toxics addition to the influent during the multi-solute activated sludge study.

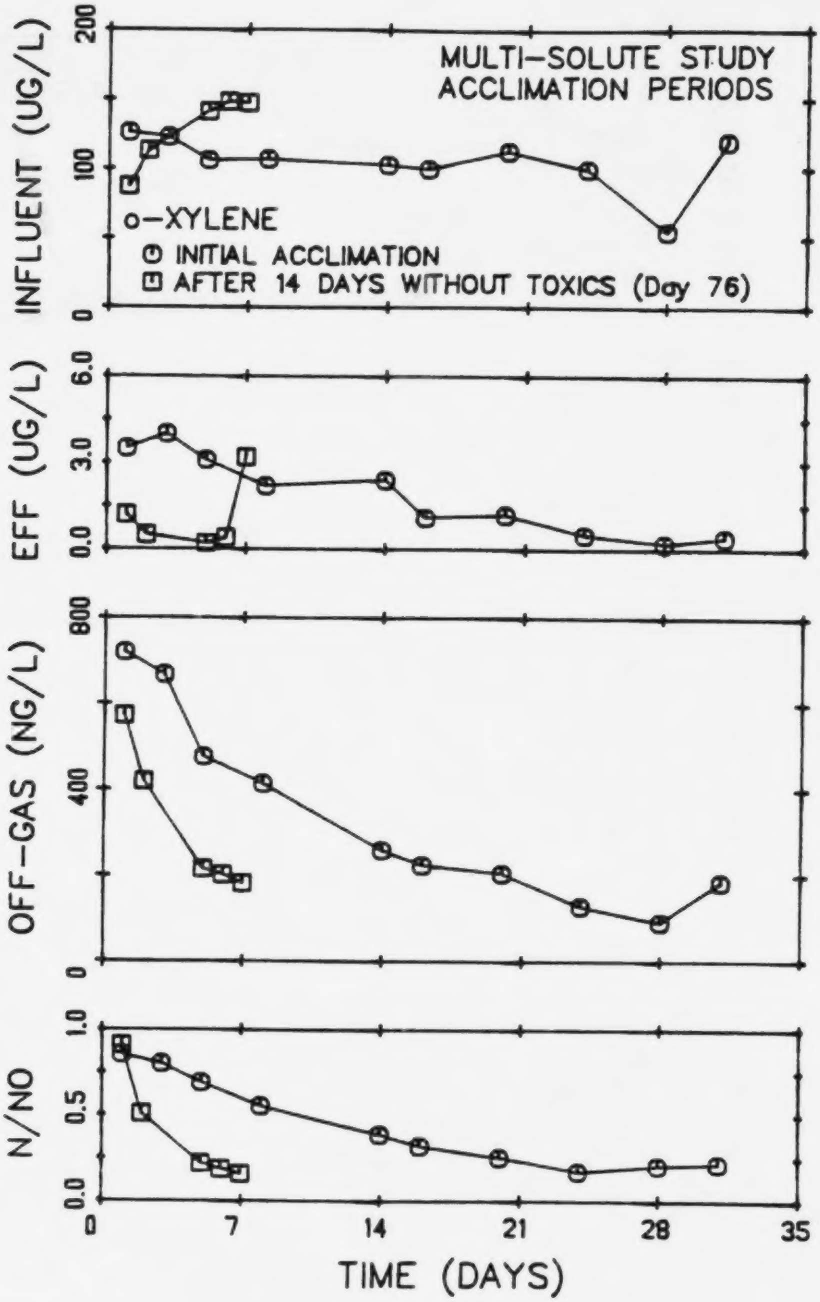


FIGURE 10-102. Initial activated sludge acclimation to o-xylene and reacclimation after a 14-day interruption in toxics addition to the influent during the multi-solute activated sludge study.

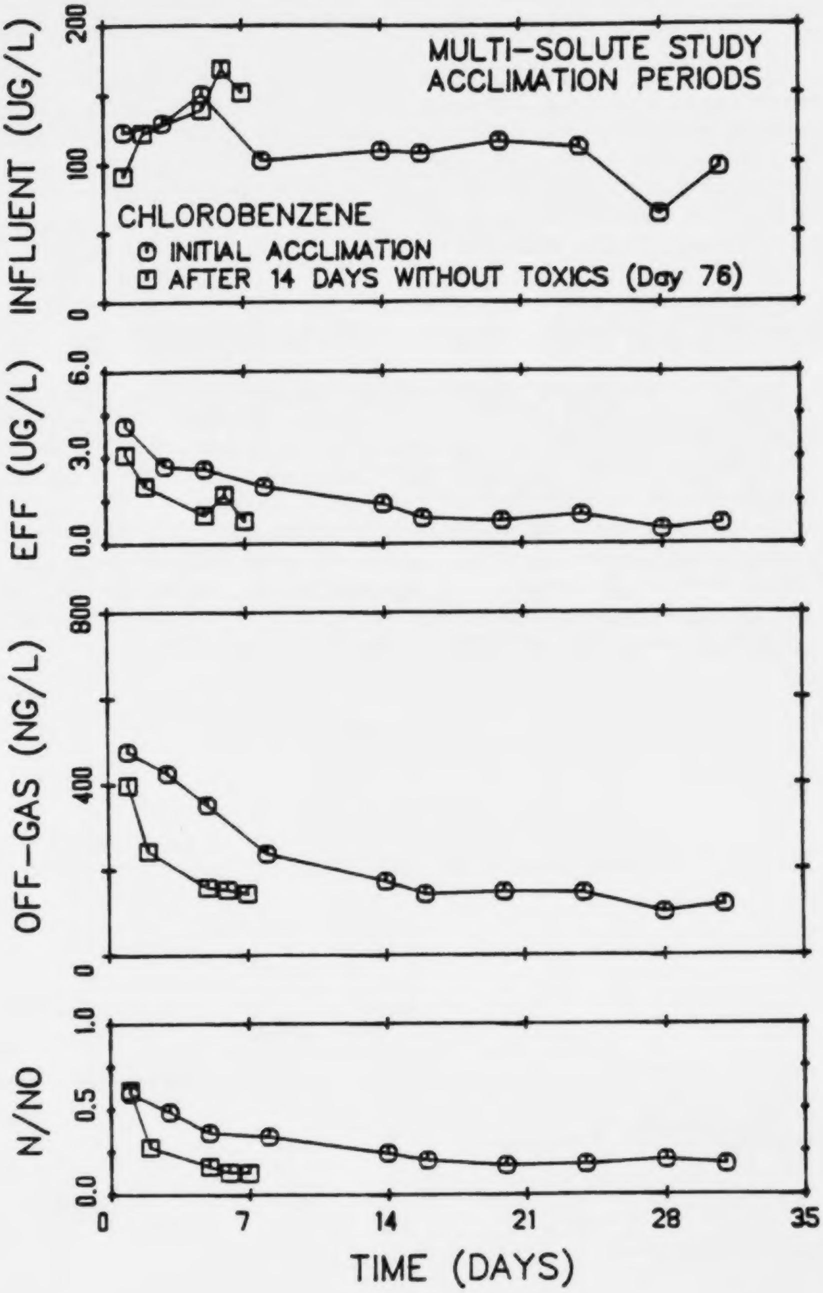


FIGURE 10-103. Initial activated sludge acclimation to chlorobenzene and reacclimation after a 14-day interruption in toxics addition to the influent during the multi-solute activated sludge study.

1,2-dichlorobenzene and 1,2,4-trichlorobenzene. Influent, effluent, and off-gas concentrations and N/N_0 values recorded for each compound during this operating period are plotted in Figures 10-104 through 10-108.

Influent concentrations of benzene, ethylbenzene, and chlorobenzene were increased from 150 μg/ℓ to over 3000 μg/ℓ for a period of five days beginning on Day 84. Influent concentrations were increased again to approximately 9000 μg/ℓ for two days, Days 90 and 91, before being returned to the 100 to 150 μg/ℓ range. The objective of this portion of the study was to evaluate what effect extremely large influent loadings of selected toxic compounds would have on the biodegradation of benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene. The highest concentrations used were slightly greater than maximum concentrations reported in influents of municipal wastewaters (2,3).

The increased toxics loadings in general had no effect on the activated sludge's ability to degrade benzene. During the operating period of high influent concentrations, Days 84-91, benzene removal due to biodegradation averaged 91% compared to 86% observed during the steady-state toxics loading period of Days 16 to 45. The maximum effluent benzene concentration recorded was 12.5 μg/ℓ (see Figure 10-104) which corresponded to the largest influent concentration of 11500 μg/ℓ. An effluent concentration of 532 μg/ℓ would be predicted by the air-stripping model to occur if the activated sludge microorganisms were not capable of degrading benzene.

TABLE 10-52

COMPARISON OF INITIAL ACCLIMATION AND REACCLIMATION AFTER 14 DAYS WITHOUT TOXICS ADDED TO THE INFLUENT

Compound	Overall Removal(%) Steady-State	Days 80-84	Acclimation Period(days) Initial	Reacclimation
Benzene	86	90	16-20	3-4
Toluene	81	88	16-20	3-4
Ethylbenzene	79	90	16-20	3-4
o-xylene	78	81	21-24	3-4
Chlorobenzene	81	86	16-20	3-4

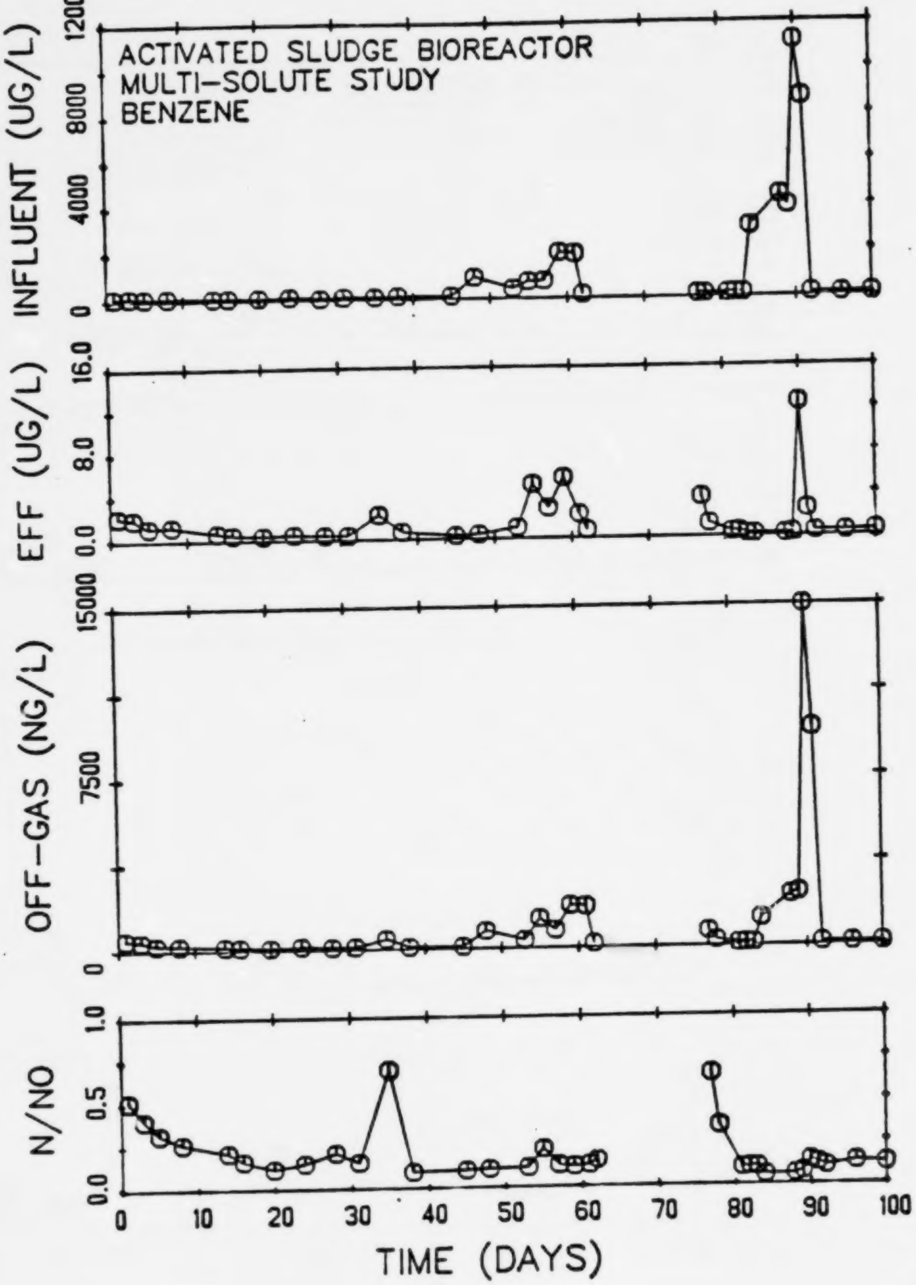


FIGURE 10-104. Effect of spike toxics loadings on benzene effluent and off-gas concentrations and fractional recoveries, N/No, during the multi-solute study.

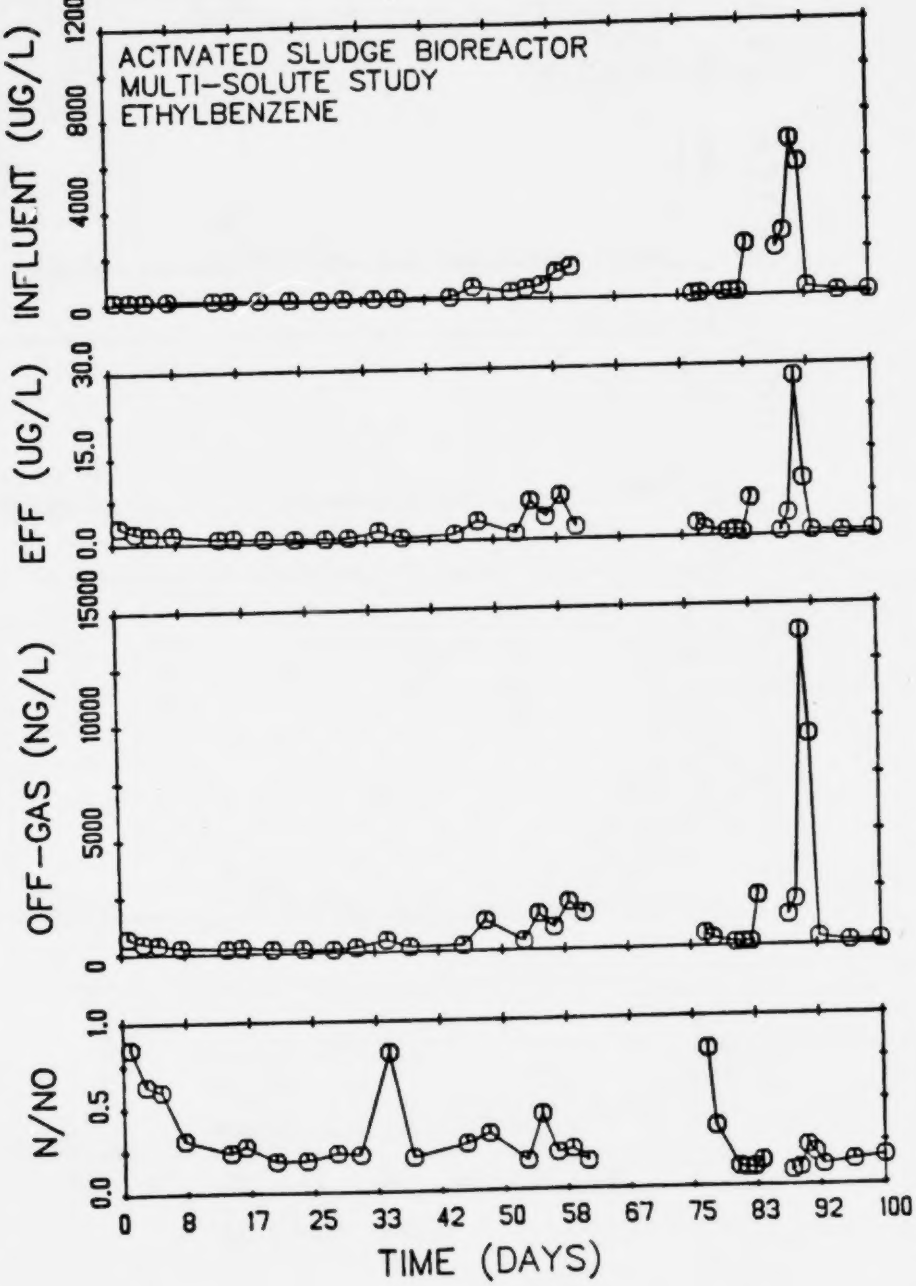


FIGURE 10-105. Effect of spike toxics loadings on ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No, during the multi-solute activated sludge study.

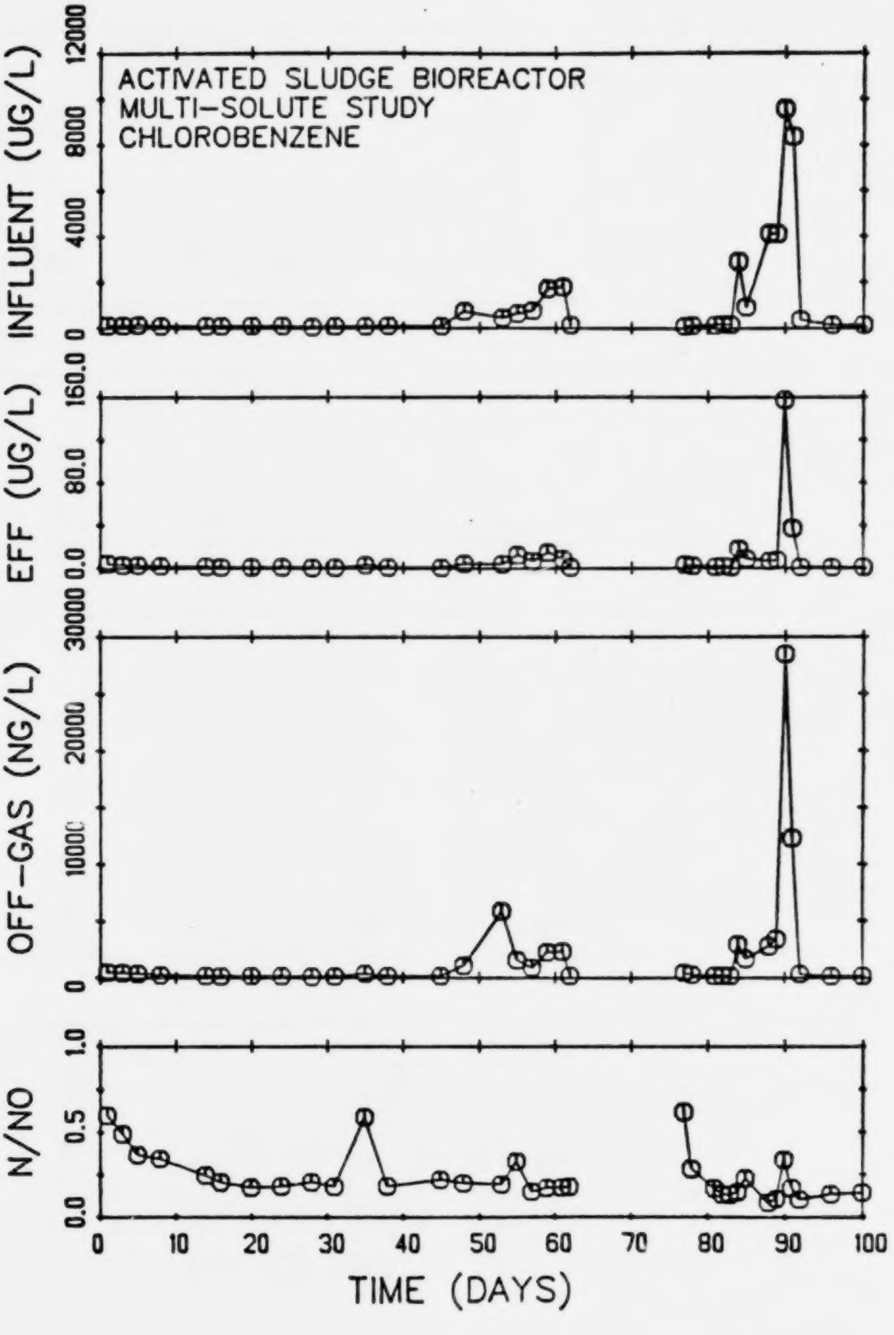


FIGURE 10-106. Effect of spike toxics loadings on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, during the multi-solute activated sludge study.

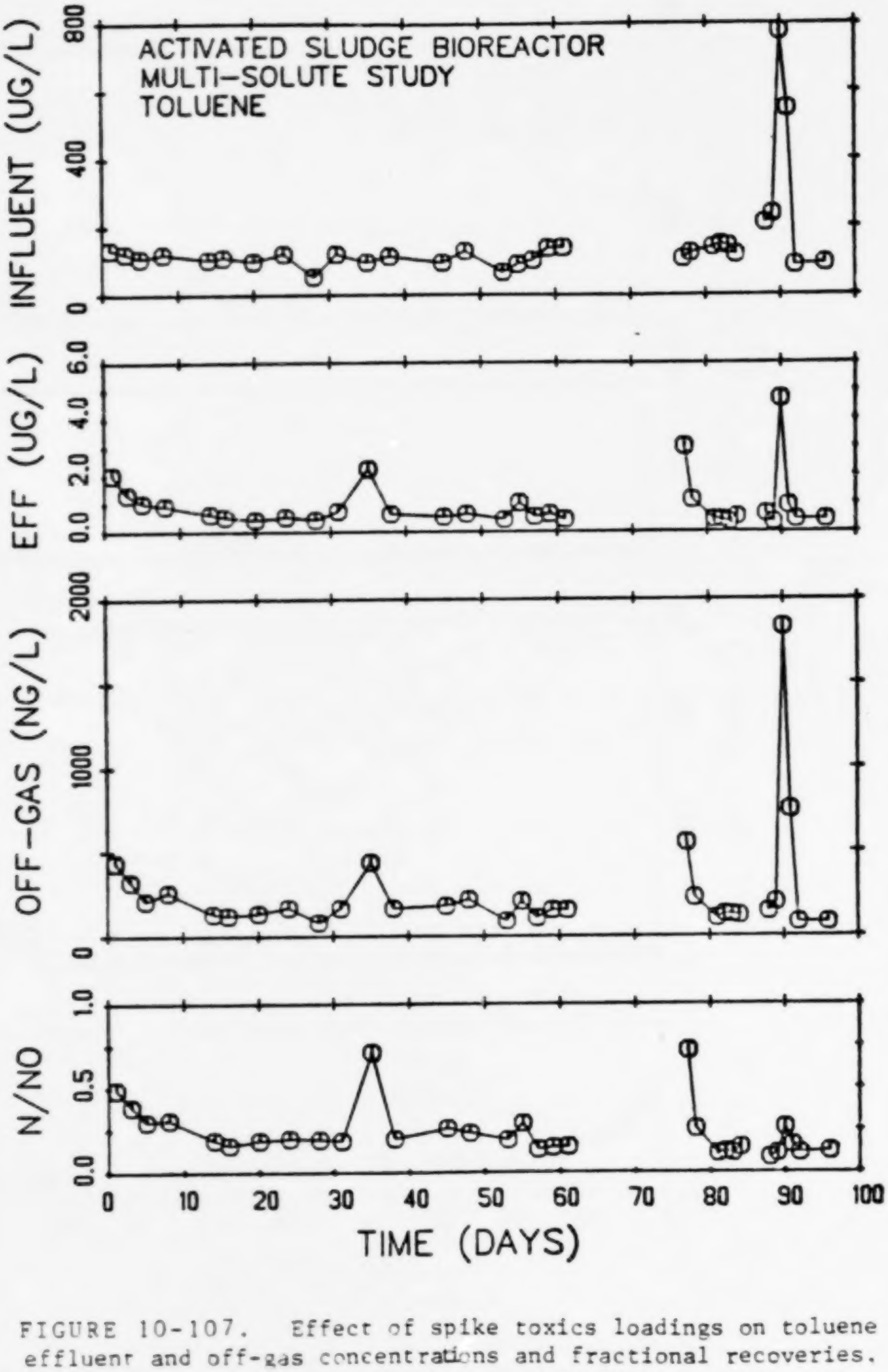


FIGURE 10-107. Effect of spike toxics loadings on toluene effluent and off-gas concentrations and fractional recoveries. N/No, during the multi-solute activated sludge study.

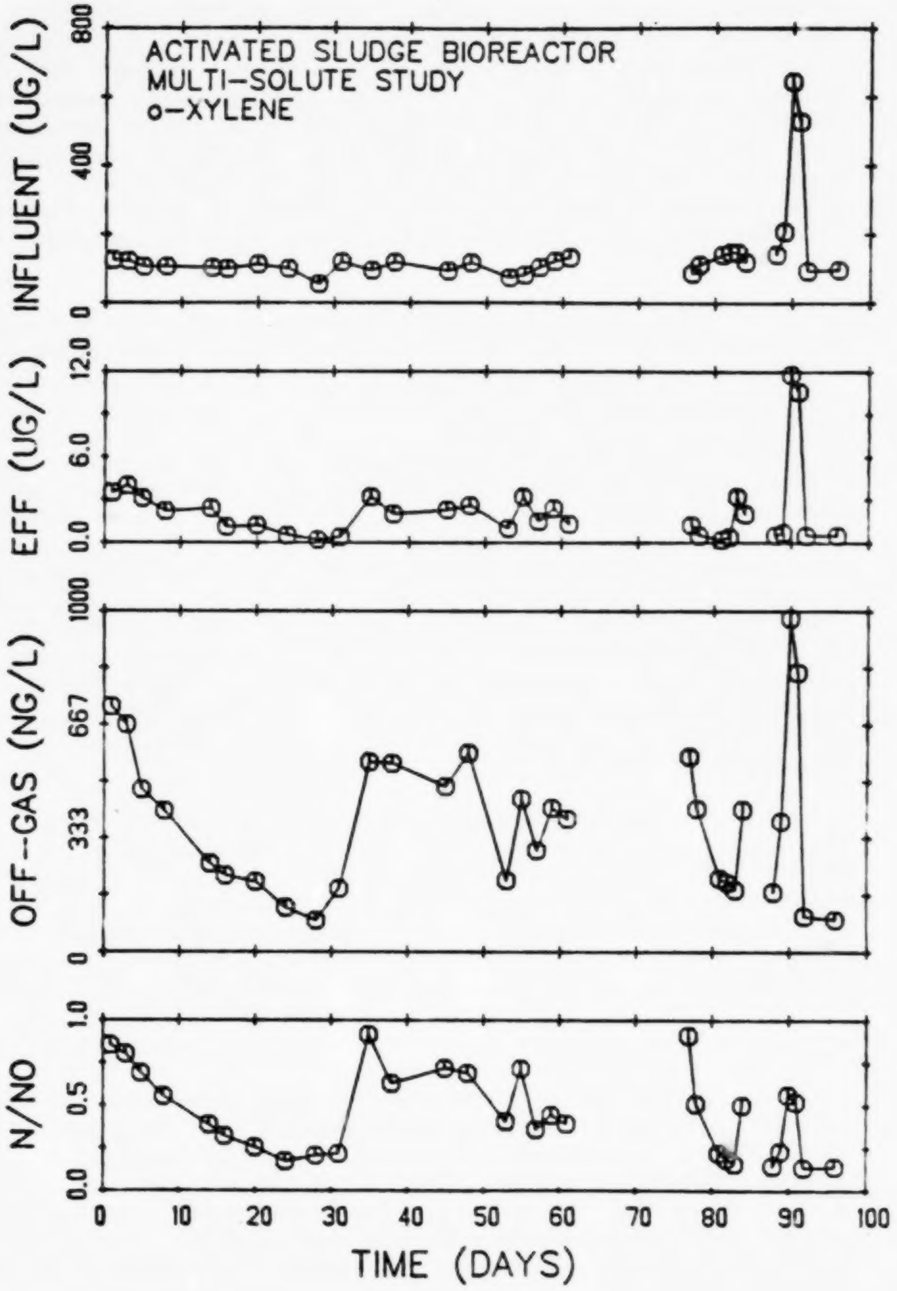


FIGURE 10-108. Effect of spike toxics loadings on o-xylene effluent and off-gas concentrations and fractional recoveries, N/No, during the multi-solute activated sludge study.

Results presented by Figure 10-105 indicate that in general the increased toxics concentrations did not adversely affect the microorganisms' ability to degrade ethylbenzene, as evidenced by the relatively constant N/N_0 values. Overall ethylbenzene removal averaged 86% during high toxics loading period, Day 84-91, compared to 80% during the steady-state loading period Day 16 to 45. Maximum effluent and off-gas concentrations of 27.7 µg/ℓ and 13700 ng/ℓ, respectively, were measured on Day 90 when the largest influent ethylbenzene concentration, 6760 µg/ℓ, was recorded. A decrease in the amount of ethylbenzene biodegraded from 90 to 80% was observed to coincide with the largest spike loading on Day 90. Overall ethylbenzene removal immediately increased during the following two days to its steady-state level of nearly 90%.

A two day period during which time no ethylbenzene was added to the influent, Day 85 to 87, had no impact upon ethylbenzene biodegradation. Overall removals measured before and after the ethylbenzene interruption period were 87 and 92%, respectively.

The chlorobenzene results reported by Figure 10-106 show slightly greater variations in biodegradative removal during the high toxics loading period than was observed for either benzene or ethylbenzene. Overall chlorobenzene removal averaged 82.6% during Days 84 to 91 compared to 81.2% during Days 16 to 45, when the influent toxics concentrations averaged approximately 100 µg/ℓ. Effluent concentrations rose from less than 1 µg/ℓ to almost 18 µg/ℓ in response to an increase in influent chlorobenzene concentration from 150 to 2900 µg/ℓ. The largest effluent concentration measured was 157 µg/ℓ which occurred on Day 90 when the influent concentration was 9560 µg/ℓ. In the absence of chlorobenzene biodegradation the effluent concentration would have been approximately 680 µg/ℓ.

The decrease in the amount of chlorobenzene removed by biodegradation from 89 to 67% on Day 90 coincided with the period of the highest influent toxics concentrations. Though the influent concentrations of all of the toxics were the same on Days 90 and 91, effluent and off-gas chlorobenzene concentrations dropped significantly between Days 90 and 91 due to an increase in microbial degradation. An effluent concentration and an overall removal of 37 µg/ℓ and 83% were recorded on Day 91, indicating a rapid return to steady-state levels.

Overall removal of toluene was largely unaffected by the high influent loadings of benzene, ethylbenzene, and chlorobenzene as evidenced by the constant N/N_0 values in Figure 10-107. The amount of toluene biodegraded averaged 86% during the steady-state loading period of Days 16 to 45. The only significant variation in biodegradative removal occurred on Day 90 when the overall removal decreased to 74%. As observed for chlorobenzene, the removal of toluene increased to approximately steady-state levels by the next sampling period on Day 91 even though influent concentrations were the same on Day 91 and Day 90.

An approximate four day period between Days 84 and 88 during which time no toluene was added to the influent had no impact on the biodegradation of toluene. Overall removals before and after the interruption in toluene addition to the bioreactor were 86 and 92%, respectively.

The results for o-xylene were significantly different than those observed for the other four biodegradable compounds. As shown by Figure 10-108, the measurable decrease in overall o-xylene removal on Day 84 coincided with increases in benzene, ethylbenzene, and chlorobenzene influent concentrations. The amount of o-xylene biodegraded decreased from 84% on Day 83 when the influent toxic concentrations were all approximately 150 μg/ℓ to 50% on Day 84. Following a four day period when o-xylene was omitted from the influent, the overall o-xylene removal increased to 85%.

The biodegradation of o-xylene was reduced on Days 90 and 91, corresponding to the highest influent toxics concentrations. Overall o-xylene removal decreased from 77% on Day 89 to only 41% on Day 90. The amount of o-xylene biodegraded increased to 48% on Day 91. Although the influent toxics concentrations were the same on Day 90 and 91, effluent toxics concentrations, especially chlorobenzene, exhibited significant reductions between Day 90 and 91. Influent and effluent o-xylene concentrations on Day 90 were 644 and 28 μg/ℓ, respectively. While the influent concentration dropped slightly on Day 91 to 529 μg/ℓ, the effluent concentration decreased by over 60% to 10 μg/ℓ as a result of the increased o-xylene biodegradation.

The influent toxics concentrations were adjusted a final time on Day 92 to the range used during the initial seven weeks of the multi-solute study, 85 to 120 μg/ℓ. Overall removals of benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene were approximately the same as observed during the steady-state biodegradation period between Days 21 and 46. As shown by the plots in Figures 10-104 through 10-108, biodegradation effected overall removals from nearly 90% for benzene and toluene to 85% for ethylbenzene and o-xylene.

Results from the multi-solute study provided valuable insight into the behavior of trace levels of toxic organic compounds during activated sludge treatment. The initial objective of the study was to compare the biodegradation of benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene in an activated sludge system receiving a variety of toxic organic compounds in the influent to the biodegradation of each compound in a system receiving only one toxic organic compound. The comparison of results from single solute studies to results from the multi-solute study demonstrated that there was no significant difference in the amount of each compound removed by biodegradation in the two systems. Steady-state biodegradation rate coefficients and acclimation phases for individual compounds in the multi-solute study were the same as those observed in single-solute studies. There were no apparent competitive interactions among the biodegradable compounds that favored biodegradation of one compound over the others.

The multi-solute study provided an excellent opportunity to observe and contrast the fate and behavior of the compounds under identical operating conditions. The consistently high recovery of 1,2,4-trichlorobenzene (generally >90%) served as an internal control to continually validate the experimental procedures used to develop mass balances on all of the compounds. In general the overall removals of the compounds were in the order predicted to occur based on results of single-solute activated sludge studies. Though not planned, the pH-upset episodes provided the opportunity to monitor the removal of each compound during an activated sludge upset period. With the exception of o-xylene, the biodegradable compounds experienced a significant, but temporary reduction in biodegradation. Within 24 to 36 hours overall removals returned to steady-state levels. The effect on o-xylene biodegradation lasted for a much longer time. In general, the biodegradation of o-xylene appeared less stable than the other four readily biodegradable compounds and more sensitive to changes in bioreactor operating conditions.

The reacclimation phase following two weeks during which time no toxics were added to the influent was only two to three days compared with the initial 14 to 21 day acclimation period at the beginning of the study. Thus, once the activated sludge had acclimated to a compound the microorganisms retained the ability to degrade it during extended periods when that compound was not found in the influent.

Increasing influent concentrations of benzene, ethylbenzene, and chlorobenzene to the 8000 to 12000 μg/ℓ range initially resulted in increased effluent concentrations of each compound and small reductions in the biodegradation of these three compounds. Reductions also occurred in the overall removal of toluene and o-xylene, which were added to the influent at 500 to 700 μg/ℓ. Within 36 to 48 hours after the adjustment in influent concentrations to the largest levels tested, the overall removal of all compounds except o-xylene approached steady-state levels. Though not studied in detail, the results suggested that the percent of each compound, except o-xylene, biodegraded increased as influent concentrations were increased from 100 to greater than 1000 μg/ℓ.

10.7 EFFECT OF INFLUENT TOXICS CONCENTRATION ON BIODEGRADATION

Activated sludge bioreactor studies were conducted to evaluate the effect of the influent toxics concentration on overall removals of four biodegradable toxics; benzene, ethylbenzene, chlorobenzene, and nitrobenzene. Studies involving the volatile compounds benzene, ethylbenzene, and chlorobenzene were conducted in bioreactors to which all three compounds were added simultaneously to the influent.

Activated sludge studies with nitrobenzene were conducted in bioreactors receiving only nitrobenzene.

The impetus for this study came from observations in the multi-solute study that overall removals and biodegradation rate coefficients generally increased as influent concentrations were increased from 100 μg/ℓ to the 500-1000 μg/ℓ range.

10.7.1 Benzene, Ethylbenzene, and Chlorobenzene

An activated sludge bioreactor study was conducted for a total of 18 weeks to examine the impact of influent concentration on the fate of three volatile, biodegradable compounds: benzene, ethylbenzene, and chlorobenzene. The 18-week study can be divided into four different operating periods, as indicated by Table 10-53, based upon the influent concentrations of the three compounds. During the first nine weeks of the study influent toxics concentrations were maintained between 15 and 30 μg/ℓ, concentrations typical of many municipal wastewaters. During the next seven weeks the influent concentrations were first increased to between 100 and 200 μg/ℓ and then to between 500 and 700 μg/ℓ. The influent concentrations were returned to the 100 to 150 μg/ℓ range during the final two weeks.

Influent, effluent, and off-gas concentrations of each toxic organic compound were measured every two to three days during the 116 days of the study. Also monitored on a regular basis were the traditional activated sludge parameters: influent and effluent soluble organic carbon (TOC), mixed liquor suspended solids (MLSS) and mixed liquor pH. Table 10-54 summarizes the TOC, MLSS, and pH data. The mean solids retention time and the hydraulic retention time were fixed at 6 days and 5.5 hours, respectively.

The fate of benzene during the first 63 days of the activated sludge study is given in Figures 10-109 and 10-110. Figure 10-109 provides measured influent, effluent, and off-gas benzene concentrations and N/N_0 values representing the fraction of the influent mass flux measured leaving the bioreactor in the effluent and off-gas combined. The concentration data in Figure 10-109 were converted to mass flux values and plotted in Figure 10-110. The dashed line representing the amount of benzene biodegraded by the activated sludge was calculated from the mass balance equation for a CMF reactor. As shown by Figure 10-109 , the effluent concentration remained less than 1.0 μg/ℓ during the 63 days when the influent concentration averaged 22.7 μg/ℓ. A significant difference between this study and activated sludge studies conducted with influent concentrations in the 100 to 200 μg/ℓ range was the absence of a distinct 14 to 21 day acclimation period characterized by a gradual decrease in N/N_0 values from approximately 0.5 to less than 0.20. Results from this study were plotted with results from an activated sludge bioreactor study with a mean influent concentration of 118 μg/ℓ in Figure 10-111. A summary of results from both studies is given by Table 10-55. For comparative purposes, the results from the

TABLE 10-53

BIOREACTOR OPERATING PERIODS IN THE ACTIVATED SLUDGE TOXICS' INFLUENT CONCENTRATION STUDY

Operating Period	Length (days)	Influent Concentrations
1. Days 0 to 63	63	15 - 30 μg/ℓ
2. Days 64 to 77	14	100 - 200 μg/ℓ
3. Days 78 to 112	35	500 - 700 μg/ℓ
4. Days 113 to 116	14	100 - 150 μg/ℓ

lower influent concentration study between days 21 and 63 were used in Table 10-55 because they represented the period of the largest benzene biodegradation. The smaller N/N_0 values from the higher influent concentration study indicated that the fraction of the influent benzene measured in the effluent and off-gas combined was less than in the low concentration study. Therefore, the percent of benzene biodegraded by the activated sludge was greater in the bioreactor with the larger influent concentration, as shown by Figure 10-111. The calculated biodegradation rate coefficient was significantly larger in the reactor operated with the higher influent concentration.

An interesting feature of the results given in Figure 10-111 and Table 10-55 were the similarities of the effluent concentrations. While mean influent concentrations differed by a factor of five, effluent concentrations were approximately the same, 0.5 μg/ℓ in the low influent concentration unit and 0.8 μg/ℓ in the higher influent concentration reactor. Based solely upon effluent concentrations the performance of the two bioreactors with respect to the amount of benzene discharged was approximately the same. Off-gas concentrations, though not identical, differed by less than a factor of three.

The results recorded for chlorobenzene during the first four weeks of the low influent concentration study were similar to those for benzene. Chlorobenzene influent, effluent, and off-gas concentrations have been plotted in Figure 10-112; mass fluxes into and out of the bioreactor are shown in Figure 10-113. Effluent, off-gas, and N/N_0 values were relatively unchanged during the first four weeks of the study. After Day 28 the fractional recovery, N/N_0, decreased indicating an increase in the amount of chlorobenzene removed by biodegradation. Corresponding to the increased biodegradative removal was a reduction in the amount of chlorobenzene leaving the bioreactor in the effluent and off-gas. The bioreactor performance with respect to overall chlorobenzene removal after Day 35 was similar to that observed in activated sludge studies with influent chlorobenzene concentrations in

TABLE 10-54

OPERATING CONDITIONS FOR THE BIOREACTOR STUDY EVALUATING THE EFFECT OF INFLUENT TOXICS CONCENTRATIONS ON BIODEGRADATION

Parameter	Mean Value
Influent TOC (mg/ℓ)	104
Effluent TOC (mg/ℓ)	17
TOC Removal (%)	84
MLSS (mg/ℓ)	3100-3400
pH	7.2
SRT (days)	6
HRT (hours)	5.5
Aeration Rate (ℓ/min)	4.1
k_v (min^{-1}), benzene	0.076
k_v (min^{-1}), ethylbenzene	0.086
k_v (min^{-1}), chlorobenzene	0.050

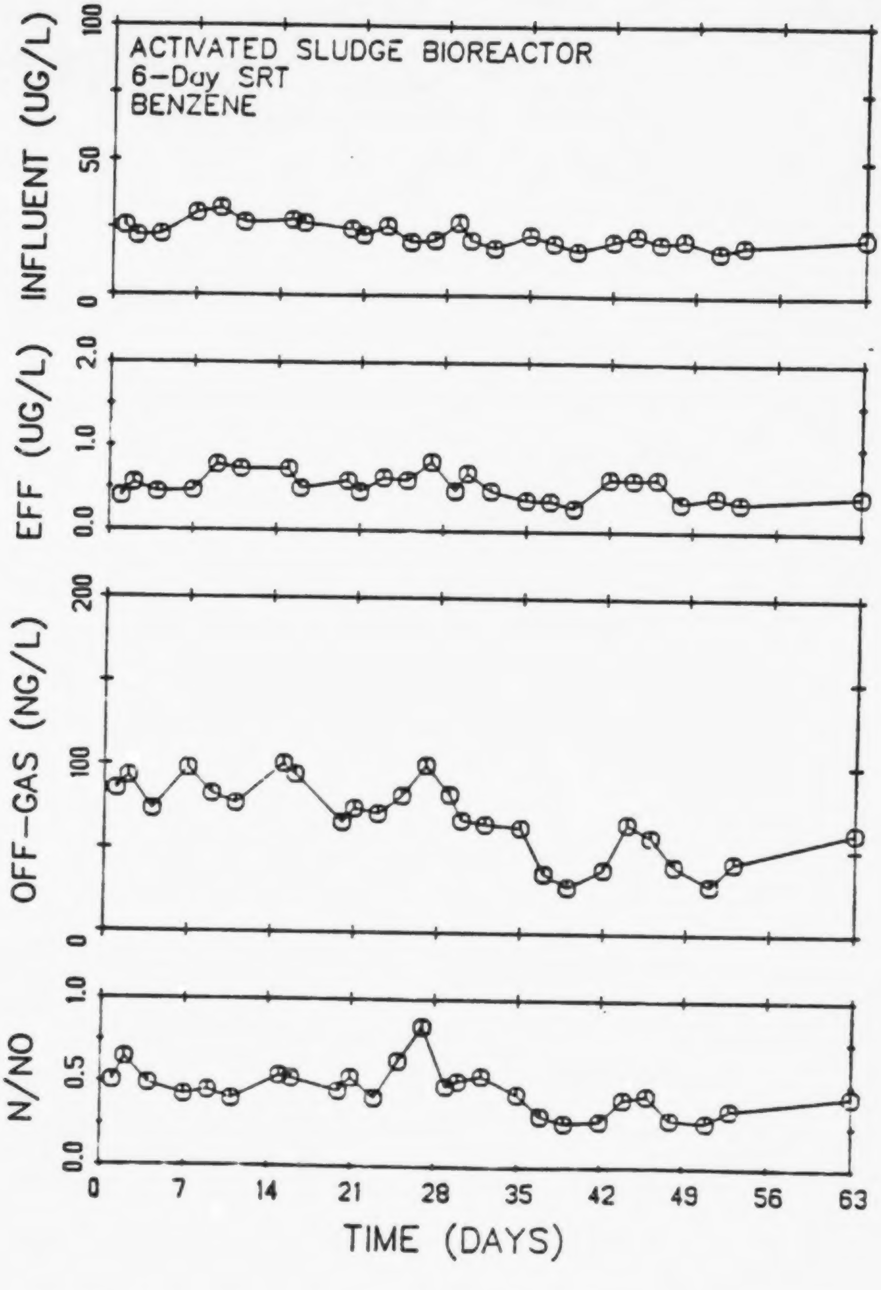


FIGURE 10-109. Benzene influent, effluent and off-gas concentrations and fractional recoveries, N/No, measured during an activated sludge study with an average influent benzene concentration of 23 ug/l.

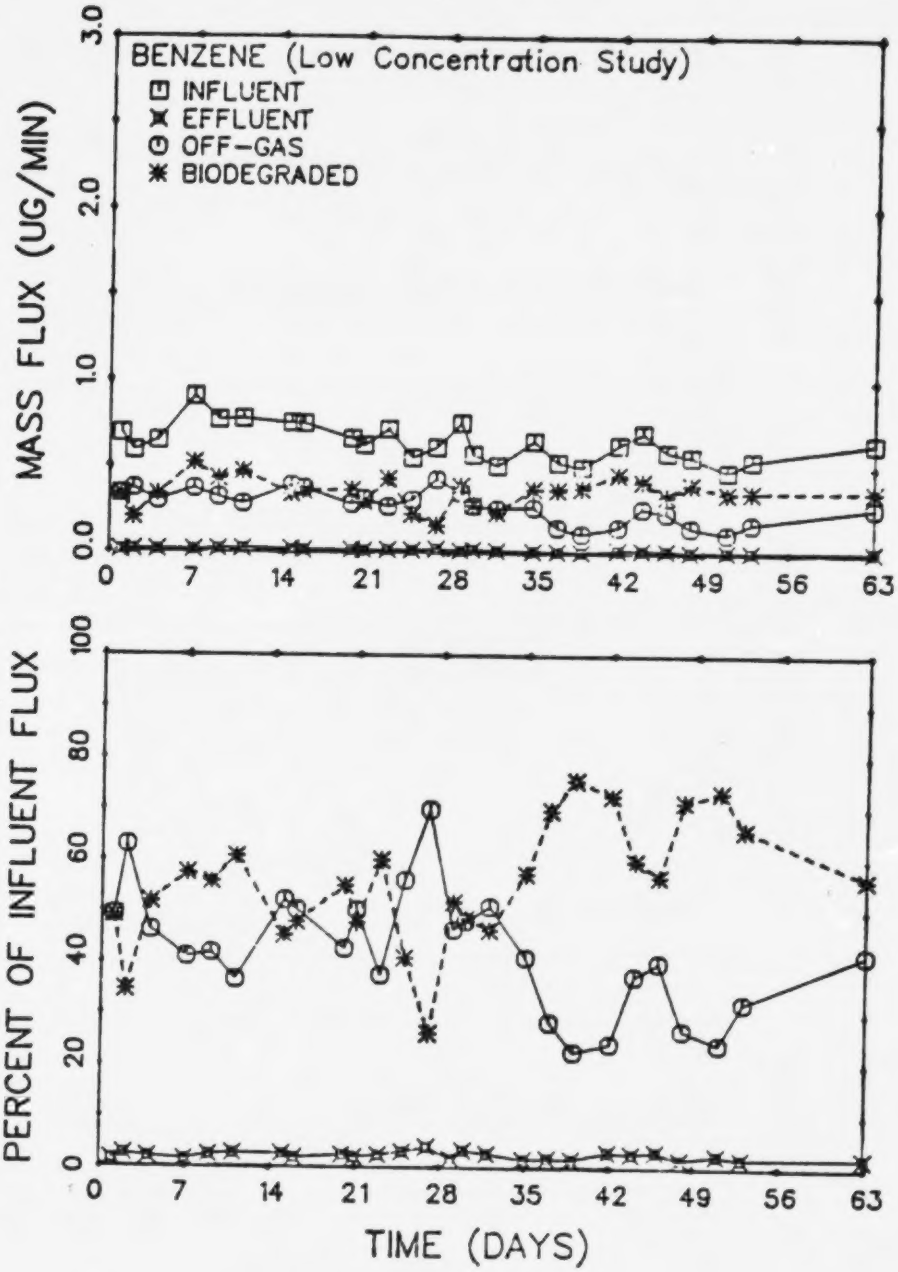


FIGURE 10-110. Benzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the activated sludge study with an average influent benzene concentration of 23 ug/l.

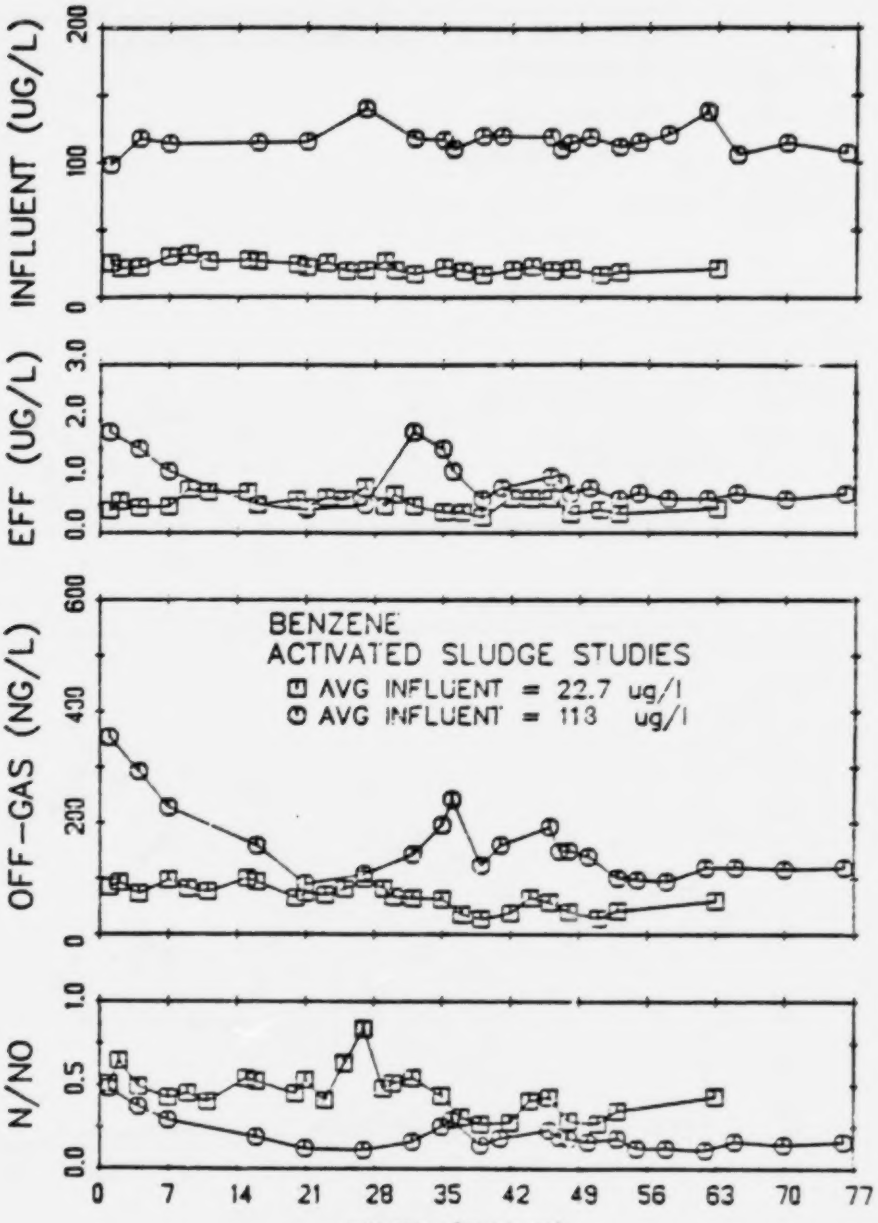


FIGURE 10-111. Comparison of benzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during activated sludge studies with average influent benzene concentrations of 23 ug/l and 118 ug/l.

TABLE 10-55

COMPARISON OF BENZENE REMOVALS IN BIOREACTORS OPERATED WITH DIFFERENT INFLUENT BENZENE CONCENTRATIONS

Parameter	Low Concentration Study (Days 21-63)	100 µg/ℓ Influent Concentration (Days 18-77)
Influent (µg/ℓ)	22.7	118
Effluent (µg/ℓ)	0.5	0.8
Off-Gas (ng/ℓ)	58.7	142
N/N_o	0.383	0.169
Overall Removal (%)	61.7	83.1
Reduction in Aqueous Concentration (%)	97.8	99.3
k_b, calculated (min^{-1})	0.124	0.507

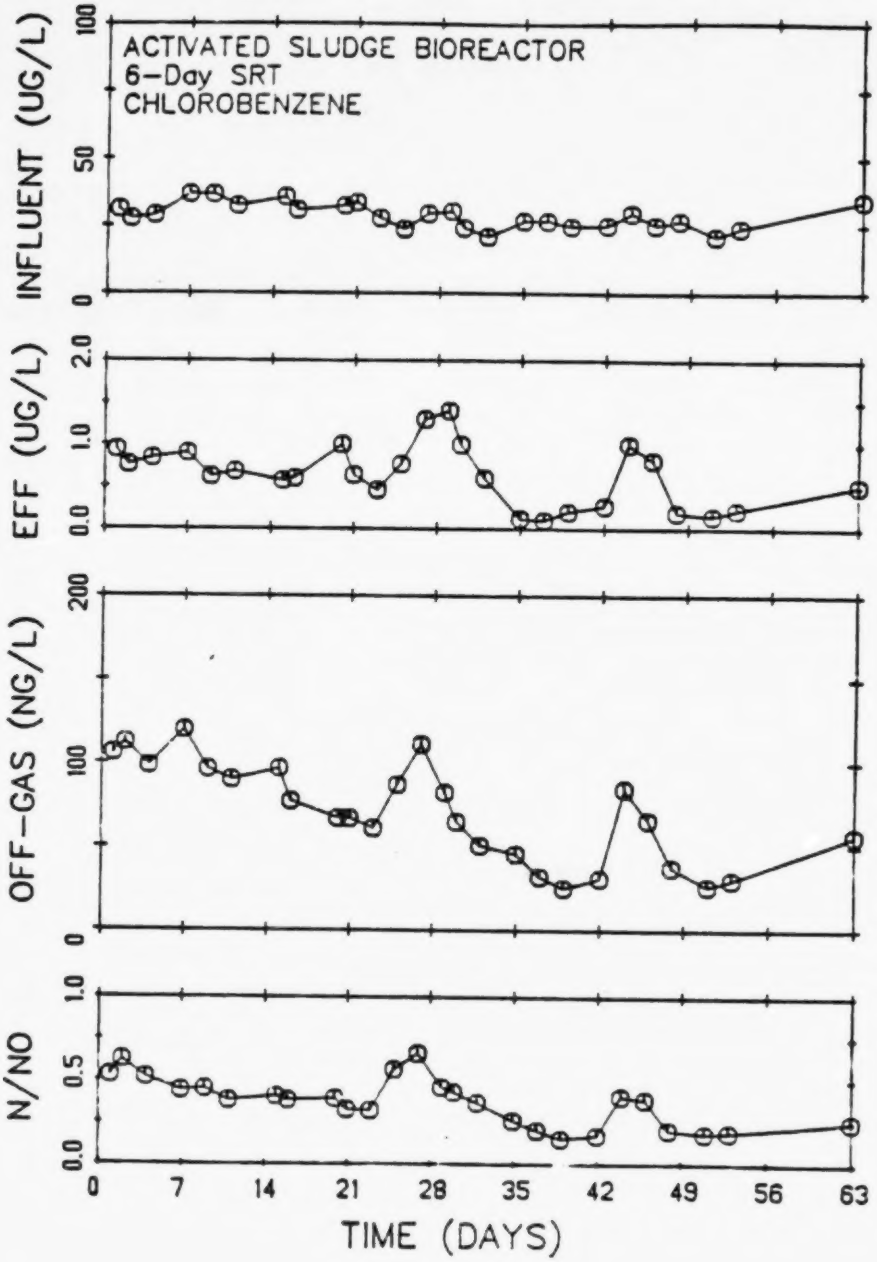


FIGURE 10-112. Chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during an activated sludge study with an average influent chlorobenzene concentration of 28 ug/l.

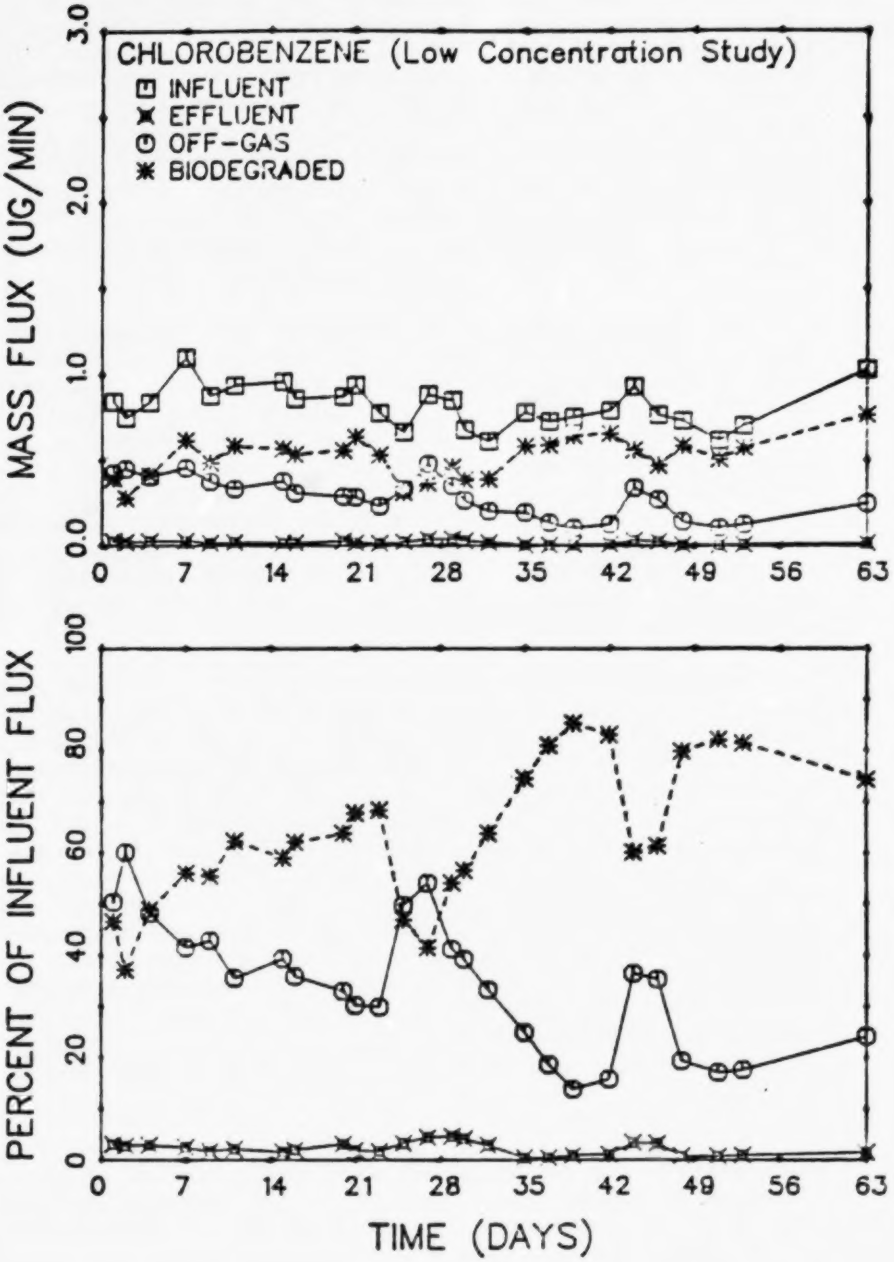


FIGURE 10-113. Chlorobenzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the activated sludge study with an average influent chlorobenzene concentration of 28 ug/l.

the 100 to 200 µg/ℓ range, as shown by the comparison in Figure 10-114. Table 10-56 summarizes and compares the results from the chlorobenzene studies compared in Figure 10-114. Results from the lower concentration study tabulated in the first column of Table 10-56 were obtained from data collected during the operating period which corresponded to the largest chlorobenzene biodegradative removal, Days 35 to 63. The values in the second column were calculated from data for the same operating period, but data collected from Days 44 to 46 were omitted. The bioreactor experienced a slight upset which caused a temporary reduction in chlorobenzene removal between Days 44 to 46. Omitting this period resulted in a slight increase in the average overall chlorobenzene removal and biodegradation rate coefficient.

The fate of ethylbenzene during the low influent concentration study is described by Figures 10-115 and 10-116 which present influent, effluent, and off-gas concentration and mass flux data, respectively. During the first eleven days the fractional recovery, N/N_0, decreased from 0.80 to approximately 0.50 where it remained for almost three weeks. The mass flux data in Figure 10-116 shows that the amount of ethylbenzene biodegraded increased substantially during the first two weeks, the primary result of which was a decrease in the amount leaving the bioreactor in the off-gas. The period of greatest biodegradation occurred from Day 35 to 63 when an average of 68% of the ethylbenzene entering the bioreactor could not be found in the effluent and off-gases combined.

Results from the low concentration study have been plotted in Figure 10-117 with results from an activated sludge study with an influent ethylbenzene concentration in the 100 to 150 µg/ℓ range. The fractional recovery of ethylbenzene from the bioreactor with the larger influent concentration was lower than that from the low influent concentration unit. This result indicated that a larger percent of the influent ethylbenzene was subject to biodegradative removal in the unit with an influent concentration between 100 and 150 µg/ℓ. The summary of the two studies in Table 10-57 shows that, like benzene, the ethylbenzene biodegradation rate coefficient, and hence overall removal, was greater in the bioreactor receiving the larger influent concentration. The effluent concentrations observed in the two studies were similar; averaging 0.3 and 0.6 µg/ℓ for the 23 and 120 µg/ℓ influent concentration bioreactors, respectively. For comparative purposes the period of greatest ethylbenzene biodegradation, Days 35 to 63, was used to compute the values in Table 10-57.

Influent, effluent, and off-gas concentrations and N/N_0 values have been compared for the following combinations of the three toxic compounds in Figure 10-118 through 10-120: benzene and ethylbenzene, benzene and chlorobenzene, and ethylbenzene and chlorobenzene, respectively. A summary of results for each compound during the last four weeks of the low concentration study, Day 35 to 63, is given in Table 10-58.

During the nine weeks of the low influent concentration period, chlorobenzene experienced the largest overall removal due to biodegradation as

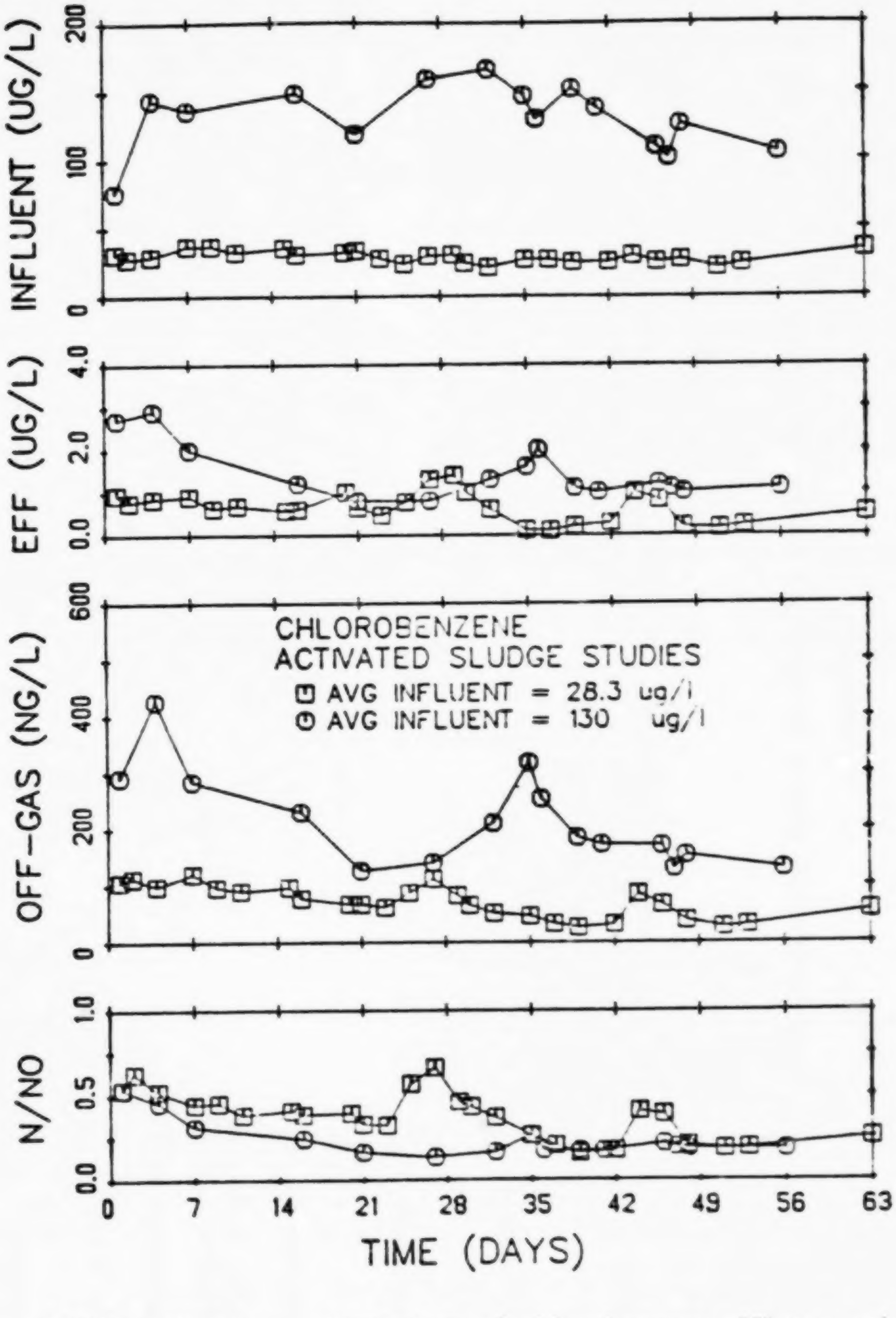


FIGURE 10-114. Comparison of chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during activated sludge studies with average influent concentrations of 28 ug/l and 130 ug/l.

TABLE 10-56

CHLOROBENZENE REMOVAL IN ACTIVATED SLUDGE BIOREACTORS

		Activated Sludge Study	
Parameter	Low Concentration Days 35-63	Low Conc. Days 35-63 (Omit Days 44-46)	100 μg/ℓ Influent Concentration (Days 16-56)
Influent (μg/ℓ)	26.6	26.3	133
Effluent (μg/ℓ)	0.4	0.2	1.1
Off-Gas (ng/ℓ)	40.4	35.6	192
N/N_o	0.243	0.200	0.180
Overall Removal (%)	75.7	80.0	82.0
Reduction in Aqueous Concentration (%)	98.5	99.2	99.2
k_b, calculated (min^{-1})	0.167	0.215	0.245

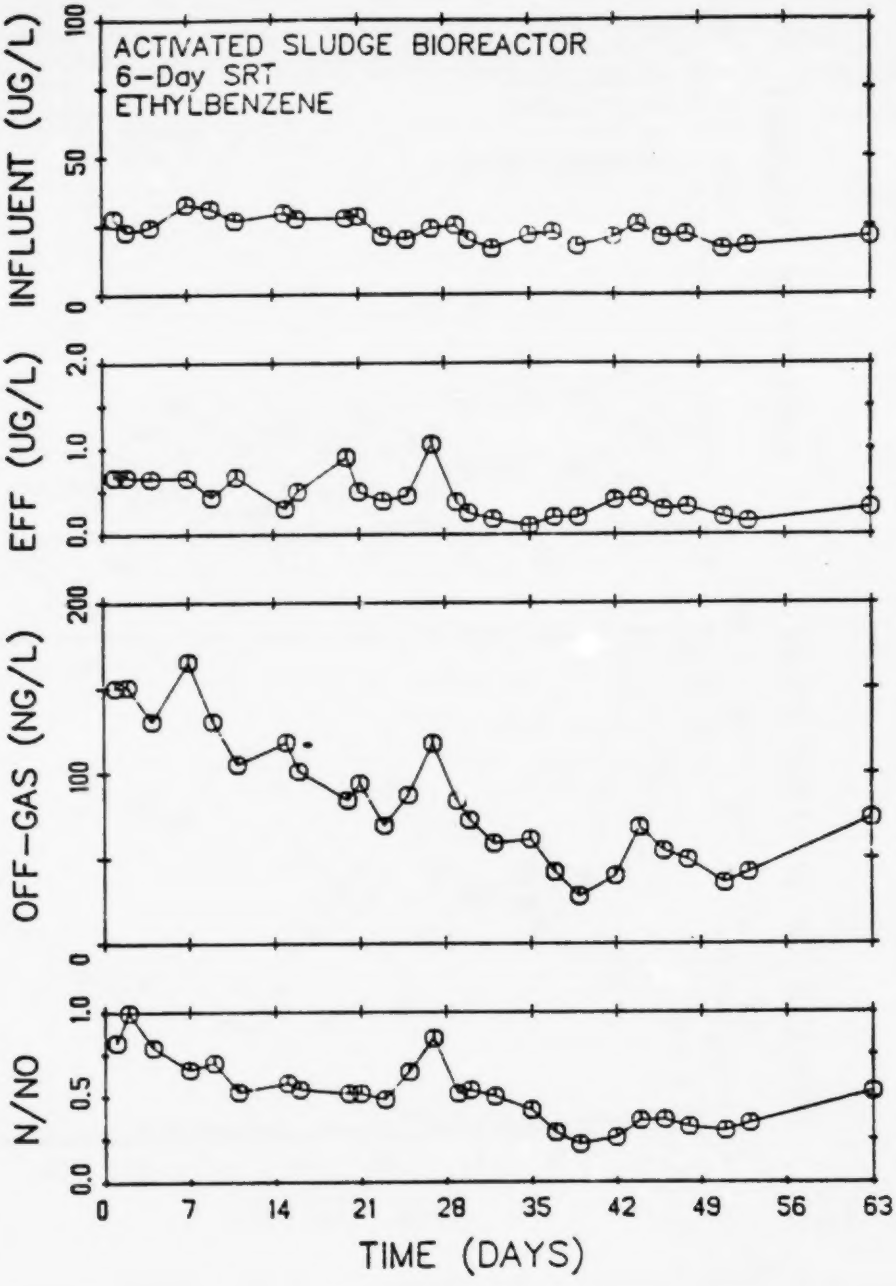


FIGURE 10-115. Ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during an activated sludge study with an average influent ethylbenzene concentration of 23 ug/l.

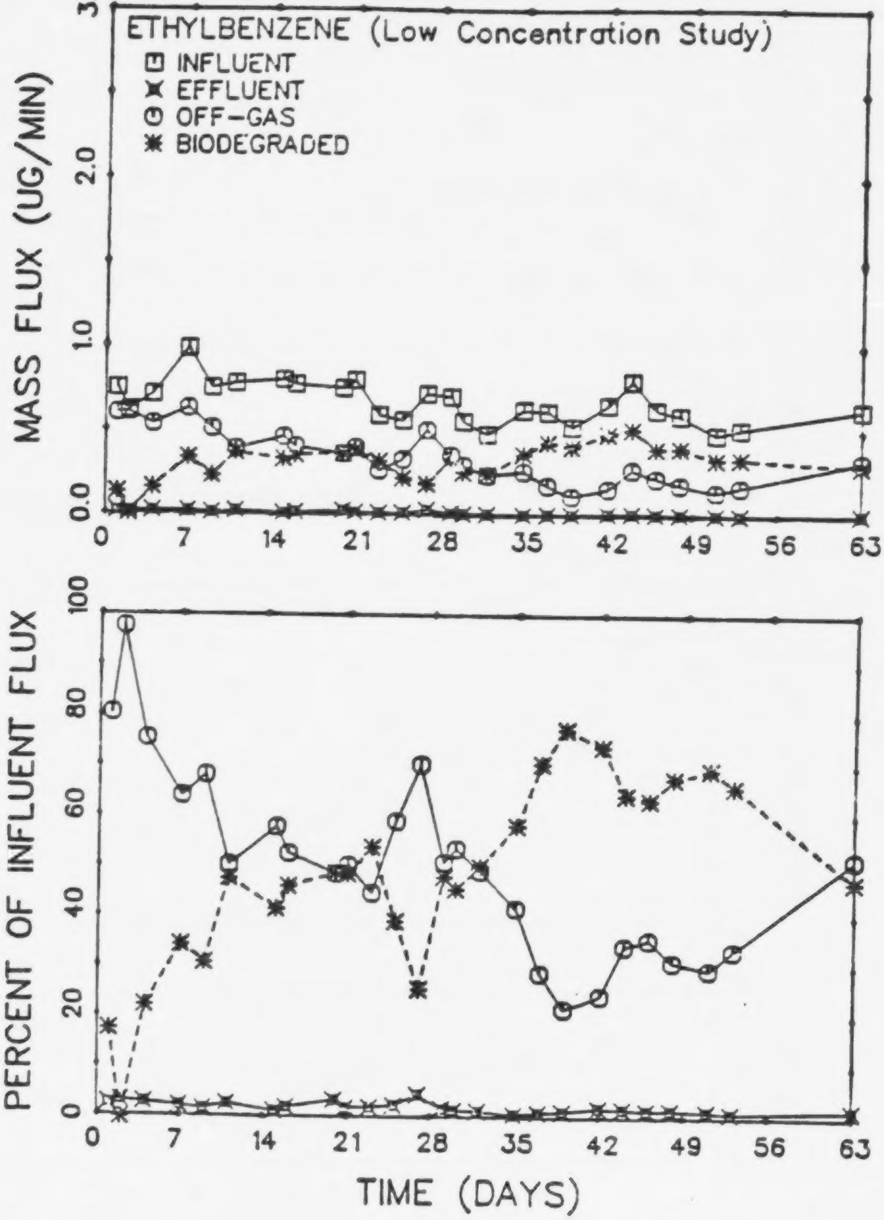


FIGURE 10-116. Ethylbenzene influent, effluent, and off-gas mass fluxes and amounts removed by biodegradation during the activated sludge study with an average ethylbenzene influent concentration of 23 ug/l.

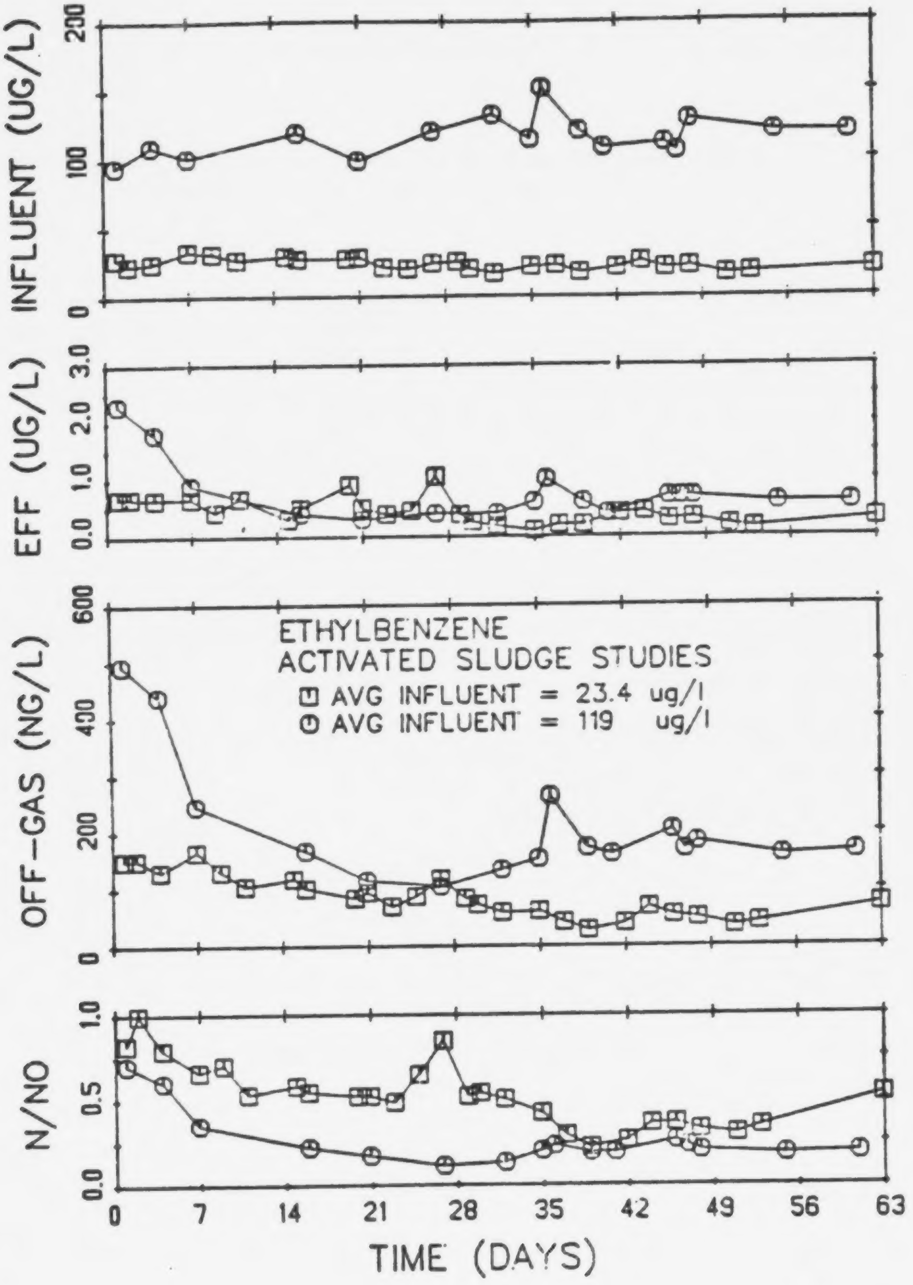


FIGURE 10-117. Comparison of ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during activated sludge studies with average influent concentrations of 23 ug/l and 119 ug/l.

TABLE 10-57

ETHYLBENZENE REMOVAL IN ACTIVATED SLUDGE BIOREACTORS WITH DIFFERENT INFLUENT TOXICS' CONCENTRATIONS

Parameter	Low Concentration Study Days 35-63	100 μg/ℓ Influent Concentration Study Days 21-63
Influent (μg/ℓ)	23.4 (6.5)	119 (14)
Effluent (μg/ℓ)	0.3 (0.1)	0.6 (0.2)
Off-Gas (ng/ℓ)	46.7 (12.9)	166 (43)
N/N_o	0.321 (0.06)	0.19 (0.04)
Overall Removal (%)	67.9	81.0
k_b, calculated (min^{-1})	0.192	0.387

( ) Standard Deviation

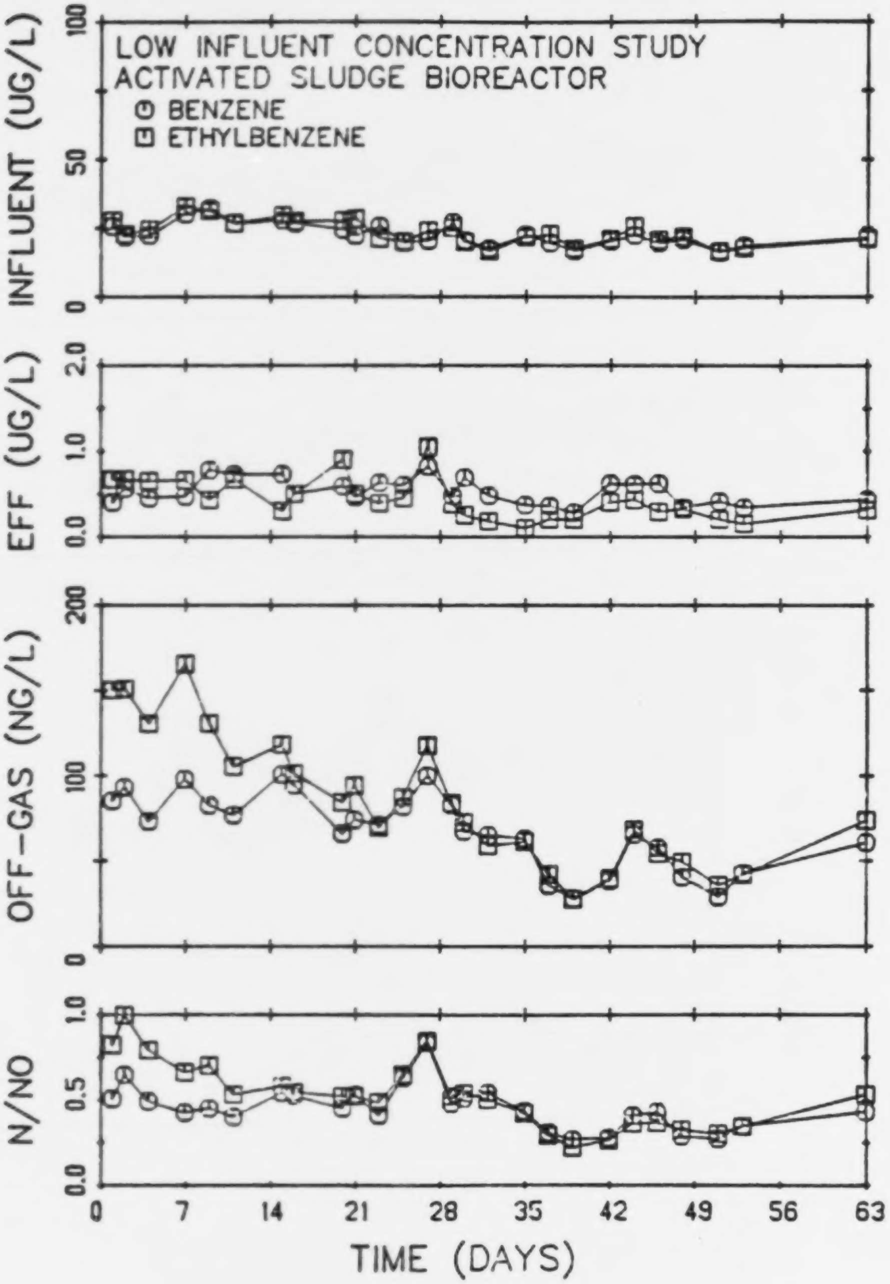


FIGURE 10-118. Comparison of benzene and ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the activated sludge study with low influent toxics concentrations.

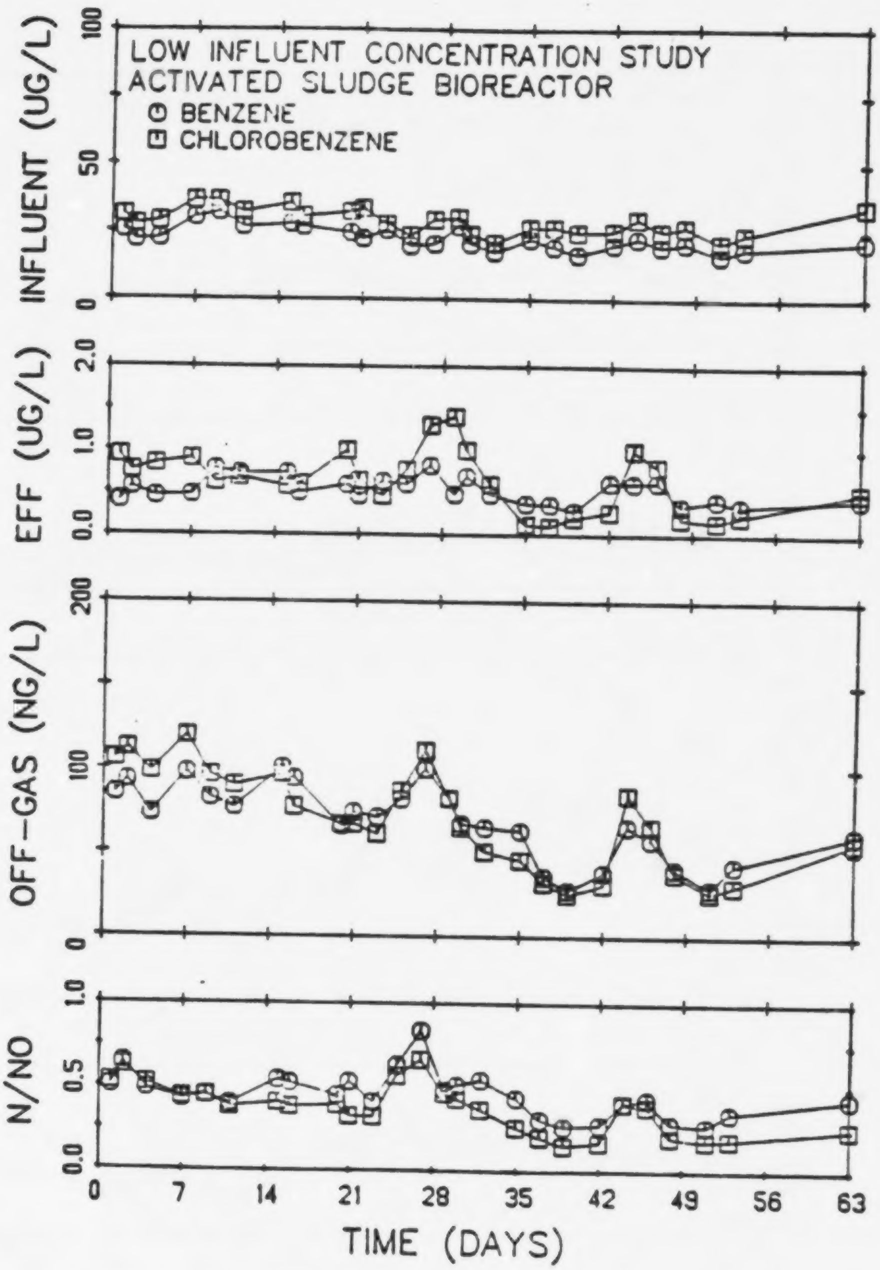


FIGURE 10-119. Comparison of benzene and chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the activated sludge study with low influent toxics concentrations.

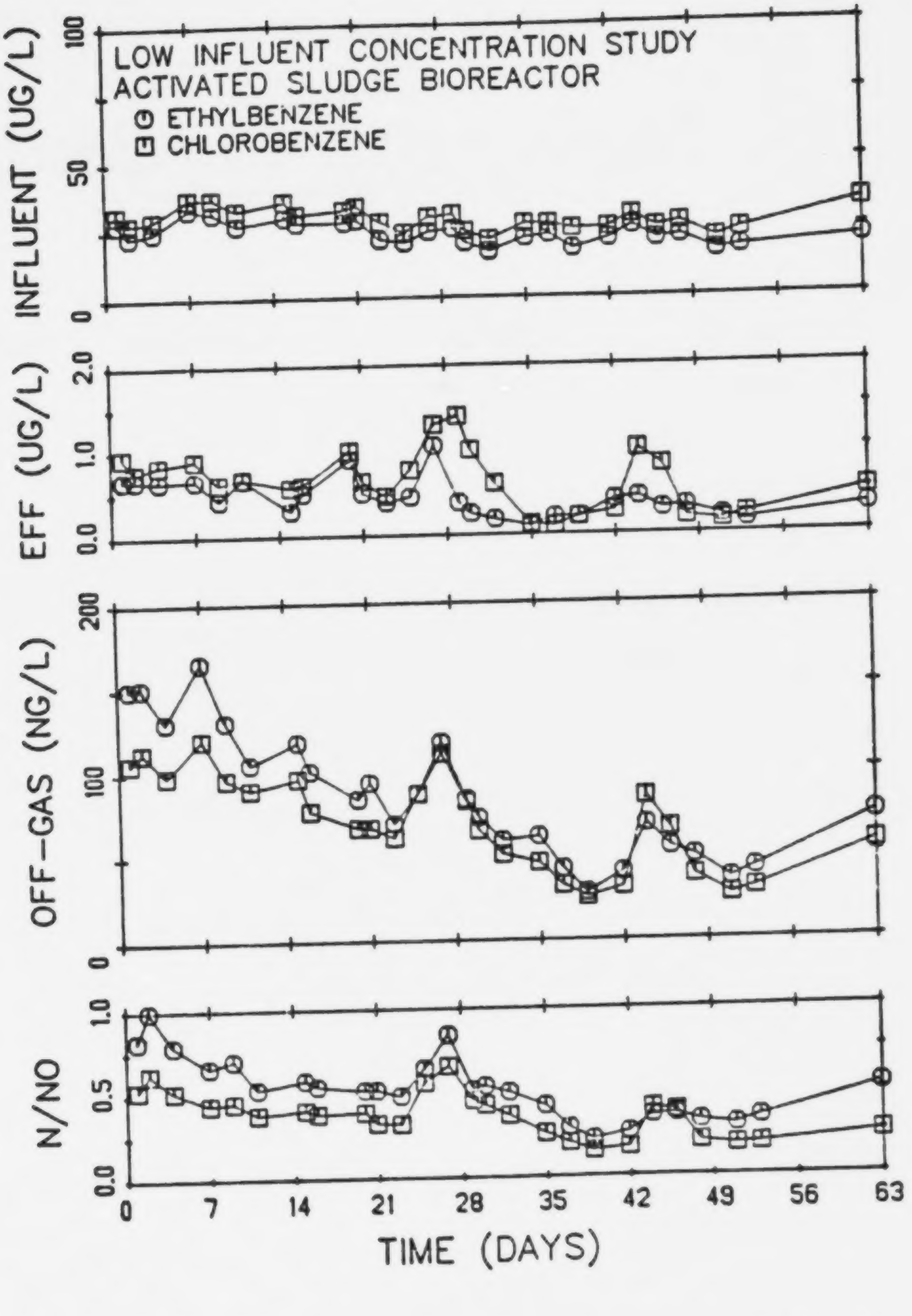


FIGURE 10-120. Comparison of ethylbenzene and chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the activated sludge study with low influent toxics concentrations.

TABLE 10-58

COMPARISON OF BENZENE, ETHYLBENZENE, AND CHLOROBENZENE REMOVALS IN THE LOW TOXICS' INFLUENT CONCENTRATION BIOREACTOR DURING DAYS 35-63

Parameter	Benzene	Ethylbenzene	Chlorobenzene
Influent (μg/ℓ)	22.7	23.4	26.6
Effluent (μg/ℓ)	0.5	0.3	0.4
Off-Gas (ng/ℓ)	58.7	46.7	40.4
N/N_0	0.383	0.321	0.243
Overall Removal (%)	61.7	67.9	75.7
Reduction in Aqueous Conc. (%)	97.8	98.6	98.5
k_b, calculated (min^{-1})	0.124	0.192	0.167
k_v (min^{-1})	0.0763	0.0878	0.0508

shown by the comparisons in Figure 10-121. Overall removal of chlorobenzene averaged nearly 76% from Day 35 to 63 compared with 62% and 68% for benzene and ethylbenzene, respectively. As shown in Table 10-59 the overall removals of benzene, ethylbenzene, and chlorobenzene in activated sludge studies with average influent concentrations in the 100 to 150 µg/ℓ were similar to each other and exceeded 80%. While biodegradation rate coefficients for the three compounds listed in Table 10-59 were different from each other when the influent concentrations were between 100 and 150 µg/ℓ, they were approximately the same when influent concentrations were in the 15 to 30 µg/ℓ range, as reported in Table 10-58.

Overall removals were calculated from N/N_o values which can be related to the volatilization and biodegradation rate coefficients as follows:

$$\frac{N}{N_o} = \frac{C_eQ_e + C_gQ_g}{C_iQ_i} = \frac{1 + k_v\bar{t}}{\bar{t}(k_b+k_v) + 1}$$

For a constant value of k_b, as k_v increases the value N/N_o increases and approaches a maximum of 1.0 which would indicate no disappearance due to biodegradation. If the values of k_b for benzene, ethylbenzene, and chlorobenzene were approximately equal, as was observed during the low concentration study, the compound with the lowest volatility should experience the greatest overall removal due to biodegradation. The mean values of k_v for benzene, ethylbenzene, and chlorobenzene during Days 35 to 63 of the low concentration study were 0.076 , 0.088 and 0.051 min^{-1}, respectively. Thus chlorobenzene would be predicted to have the greatest overall removal and lowest fractional recovery.

The influent concentration of each compound was increased from the 15 to 30 µg/ℓ range to the 100 to 200 µg/ℓ range on Day 64 and maintained at that level for approximately two weeks. On Day 78 the influent concentrations were further increased to between 600 and 700 µg/ℓ where they remained for three weeks. During the last two weeks of the study the influent concentrations were reduced to approximately 100 µg/ℓ.

The results for benzene, shown by Figure 10-122, indicated that the decrease in fractional recovery, N/N_o, coincided with the operating period of increased influent concentrations. The mean N/N_o value decreased from 0.32, averaged during the low influent phase between Days 35 and 63, to 0.08 for the operating period from Day 79 to 101 indicating that the biodegradation rate had increased. Table 10-60 gives mean values for influent, effluent, and off-gas concentrations and overall removals recorded during periods of low, 22.7 µg/ℓ, and high, 601 µg/ℓ, influent concentrations. A significant finding was that only a small increase in the effluent concentration resulted from the increased influent concentration. The largest effluent concentration

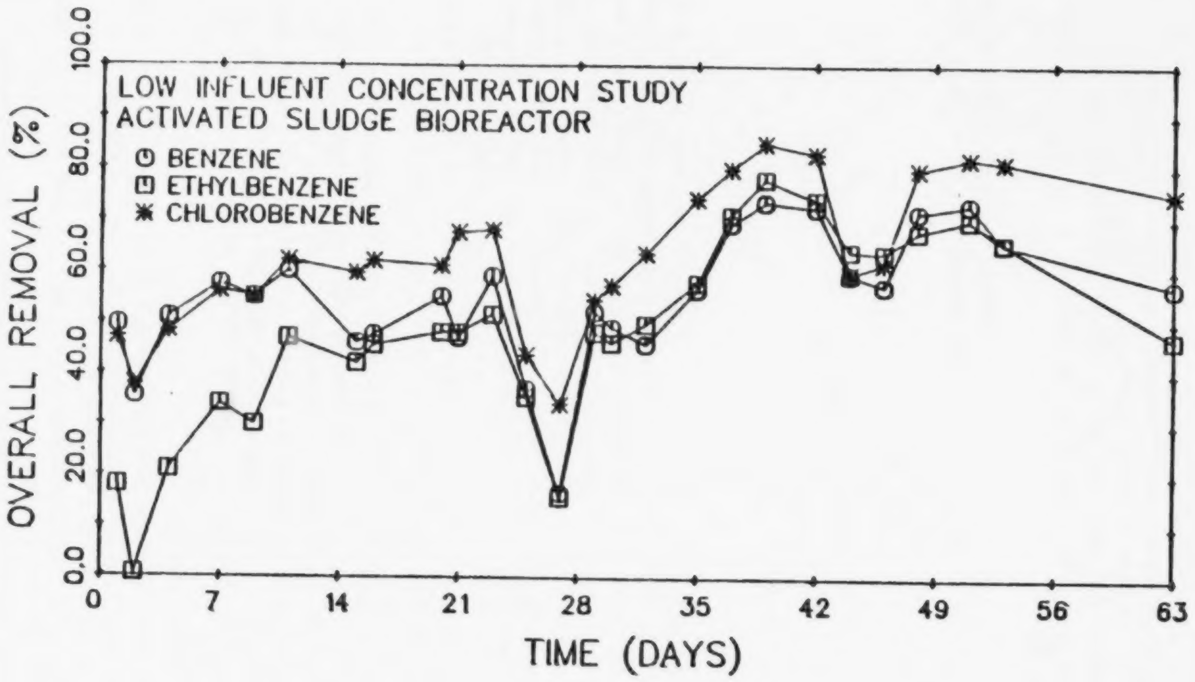


FIGURE 10-121. Comparison of benzene, ethylbenzene, and chlorobenzene overall removals due to biodegradation during the activated sludge study with low influent concentrations.

TABLE 10-59

COMPARISON OF STEADY-STATE REMOVALS OF BENZENE, ETHYLBENZENE, AND CHLOROBENZENE IN SINGLE SOLUTE ACTIVATED SLUDGE STUDIES

Parameter	Benzene	Ethylbenzene	Chlorobenzene
Influent (μg/ℓ)	118	119	133
Effluent (μg/ℓ)	0.8	0.6	1.1
Off-Gas (ng/ℓ)	142	165	192
N/N_o	0.169	0.190	0.180
Overall Removal (%)	83.1	81.0	82.0
Reduction in Aqueous Conc. (%)	99.3	99.5	99.2
k_b, calculated (min^{-1})	0.51	0.387	0.245

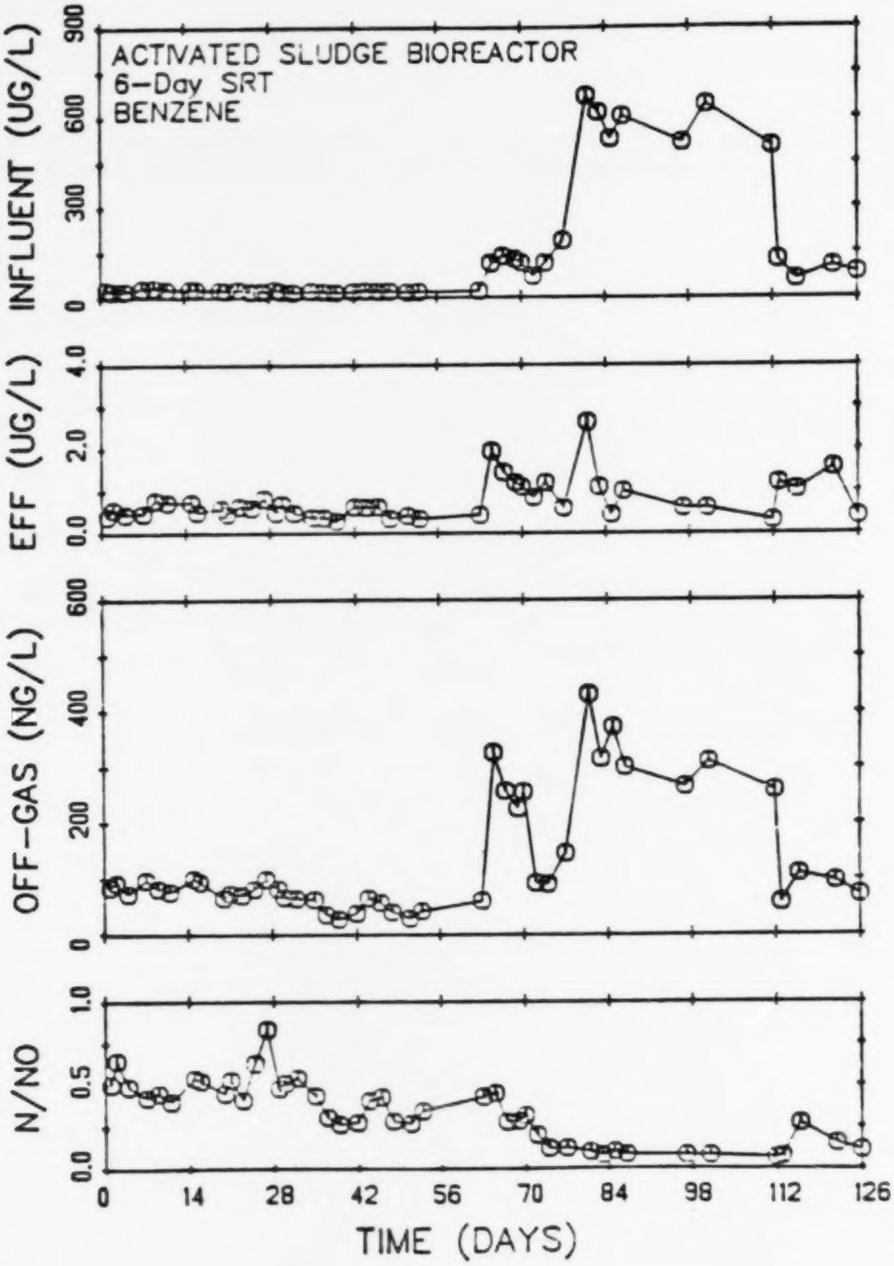


FIGURE 10-122. Effect on effluent and off-gas concentrations and fractional recoveries, N/No, of 10 to 30-fold increases in influent benzene concentration to the activated sludge bioreactor receiving a 23 ug/l average influent benzene concentration.

TABLE 10-60

EFFECT OF INFLUENT CONCENTRATION ON THE REMOVAL OF BENZENE FROM AN ACTIVATED SLUDGE BIOREACTOR

Parameter	Days 35-63+	Days 79-101++
Influent (μg/ℓ)	22.7	601 (64.6)
Effluent (μg/ℓ)	0.5	1.0 (0.7)
Off-Gas (ng/ℓ)	58.7	323 60.6)
N/N_o	0.383	0.081 (0.011)
Overall Removal (%)	61.7	91.9
Reduction in Aqueous Conc. (%)	97.8	99.8
k_b (min^{-1})	0.124	0.919

+ Values averaged from 9 samples collected over 28 days

++ Values averaged from 8 samples collected over 22 days

( ) Numbers in parentheses are standard deviations recorded was less than 2.5 μg/ℓ, and it occurred one day after the influent concentration was increased from 200 to 650 μg/ℓ. An interesting feature of the results in Figure 10-122 was the variation in both effluent and off-gas concentrations between Days 64 and 77. While the influent concentration during that operating period was relatively constant with an average value of 124 μg/ℓ, the effluent and off-gas concentrations decreased significantly. The calculated biodegradation rate coefficient increased from less than 0.20 to greater than 0.90 min^{-1} during this period.

The greatest overall removal of benzene during the 18 weeks of the study occurred during the period of the highest influent concentration, Days 81 to 101. Overall benzene removal due to biodegradation averaged 92% during that period compared with only 62% during Days 35 to 63 of the low influent concentration period.

Ethylbenzene behaved in a manner similar to benzene as shown by the results in Figure 10-123. A decrease in the mean fractional recovery of ethylbenzene from 0.33 to 0.08 coincided with the period of increased influent concentrations. While little variation in the steady-state effluent concentrations occurred as a result of the change in influent concentration, off-gas concentrations increased measurably.

The ethylbenzene results in Figure 10-123 between Days 64 and 77 exhibited the same trend as observed for benzene. Following initial increases on Day 64 caused by the change in influent concentration, the effluent and off-gas concentrations decreased by a factor of four over the next two weeks. The corresponding reduction in fractional recoveries indicated a further acclimation of the activated sludge to ethylbenzene and an increased biodegradation rate. Table 10-61 summarizes mean influent, effluent, and off-gas concentrations, overall removals, and biodegradation rate coefficients recorded during the low and high influent concentration periods.

The fractional recovery of chlorobenzene decreased from a mean value of 0.24 recorded during the operating period Day 35 to 63 to 0.07 for the period of highest influent toxics concentrtions, Days 79 to 101 as shown by the results presented in Figure 10-124 and summarized by Table 10-62.

Effluent concentrations showed initial increases coinciding with the increased influent concentrations, but then decreased to approximate steady state levels within ten days. The increase in influent chlorobenzene concentration on Day 64 produced a five fold increase in off-gas concentration. While the influent concentration averaged approximately 140 μg/ℓ for the operating period Days 64 to 77, the off-gas concentration decreased by over 50% as the chlorobenzene biodegradation rate increased.

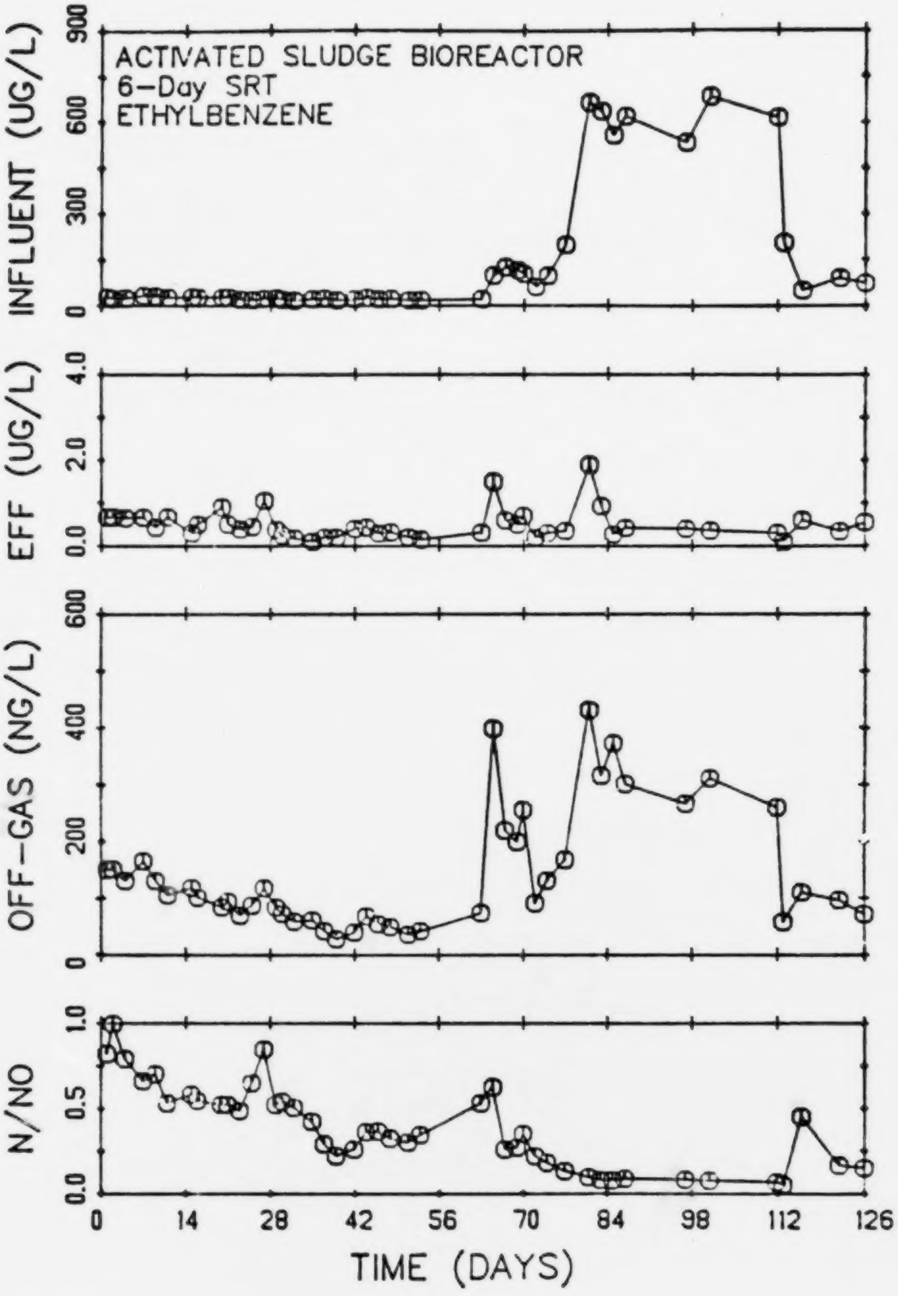


FIGURE 10-123. Effect on effluent and off-gas concentrations and fractional recoveries, N/No, of 10 to 30-fold increases in influent ethylbenzene concentration to the activated sludge bioreactor receiving a 23 ug/l average ethylbenzene concentration.

TABLE 10-61

EFFECT OF INFLUENT CONCENTRATION ON THE REMOVAL OF ETHYLBENZENE FROM AN ACTIVATED SLUDGE BIOREACTOR

Parameter	Days 35-63	Days 79-101
Influent (μg/ℓ)	20.7	617 (49.7)
Effluent (μg/ℓ)	0.3	0.7 (0.6)
Off-Gas (ng/ℓ)	48.1	331 (44.1)
N/N_o	0.332	0.079 (0.01)
Overall Removal (%)	66.8	92.1
Reduction in Aqueous Conc. (%)	98.6	99.9
k_b (min^{-1})	0.183	1.081

( ) Standard Deviation

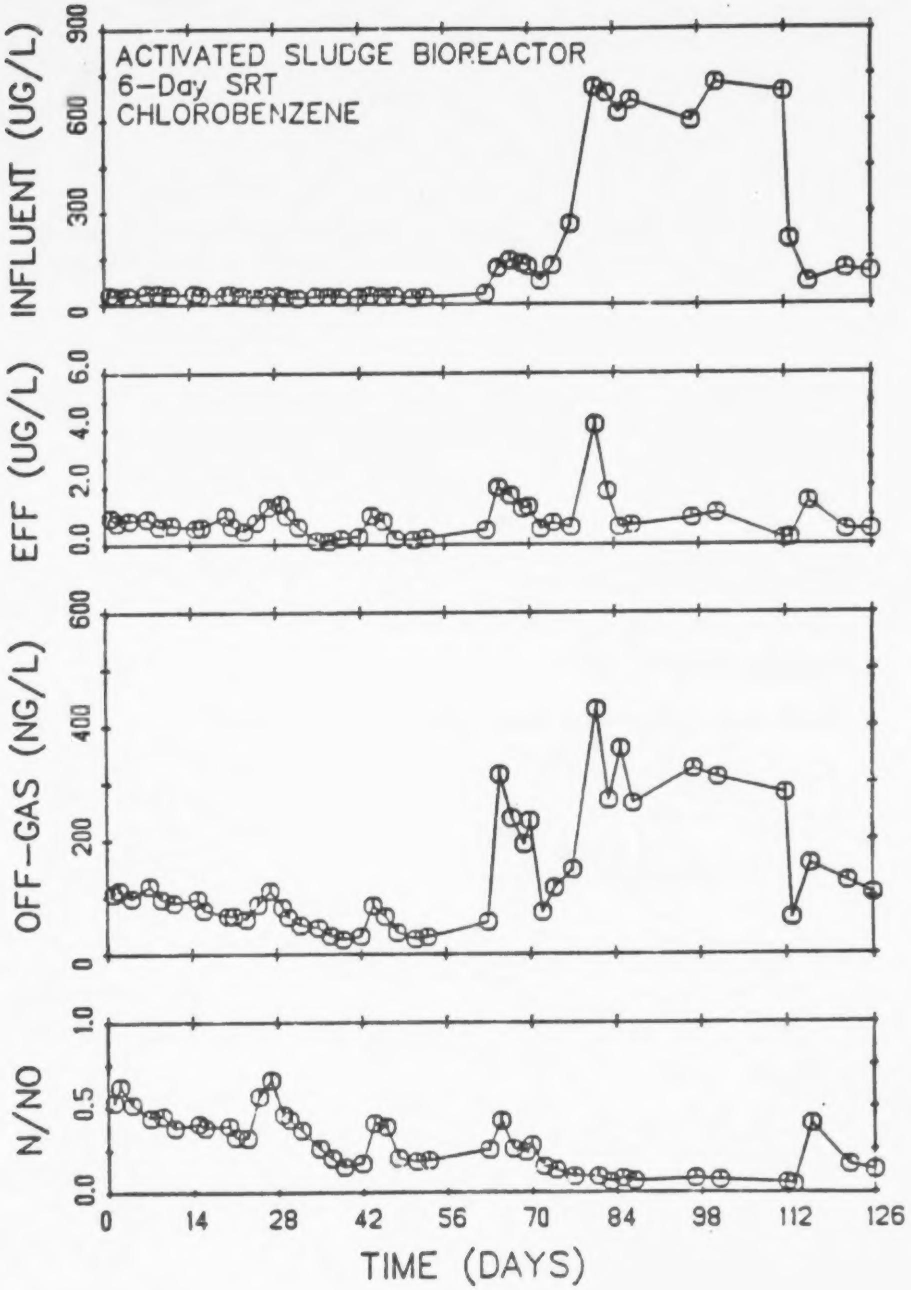


FIGURE 10-124. Effect on effluent and off-gas concentrations and fractional recoveries, N/No, of 10 to 30-fold increases in influent chlorobenzene concentrations to the activated sludge bioreactor receiving a 28 ug/l average influent chlorobenzene concentration.

TABLE 10-62

EFFECT OF INFLUENT CONCENTRATION ON THE REMOVAL
OF CHLOROBENZENE FROM AN ACTIVATED SLUDGE BIOREACTOR

Parameter	Days 35-63	Days 79-101
Influent (μg/ℓ)	26.6	673 (41.6)
Effluent (μg/ℓ)	0.4	1.3 (1.3)
Off-Gas (ng/ℓ)	40.4	331 (43.9)
N/N_o	0.243	0.071 (0.013)
Overall Removal (%)	75.7	92.9
Reduction in Aqueous Conc. (%)	98.5	99.8
k_b, calculated (min^{-1})	0.167	0.719

( ) Standard Deviation

Overall removals of benzene, ethylbenzene, and chlorobenzene attributed to biodegradation have been plotted in Figure 10-125 for the 18 weeks of the bioreactor study. The results show the significant increase in removals measured during the first 63 days when influent concentrations ranged from 15 to 30 μg/ℓ compared to those measured between Days 79 and 112 when influent concentrations ranged from 600 to 650 μg/ℓ. Average overall removals during the low concentration period were largest for chlorobenzene, 75%, compared to approximately 66% for both benzene and ethylbenzene. Overall removals of each compound were equivalent for the three compounds and averaged 92% during the operating period when influent concentrations averaged greater than 600 μg/ℓ. The relatively horizontal lines describing removal between Day 79 and 112 indicated a larger degree of stability with respect to toxics biodegradation than was observed during the preceding period of low influent concentrations.

An important finding of this study was the activated sludge microorganisms' ability to degrade the three organic compounds to low part-per-billion levels. Influent concentrations in the 15 to 30 μg/ℓ range represent typical levels of organic priority pollutants that occur in municipal wastewaters. The bacteria exhibited an ability to degrade the compounds even though the concentration to which they were exposed, the effluent concentration in a CMF reactor, never exceeded approximately 1.5 μg/ℓ. Effluent or mixed liquor concentrations typically were less than 1.0 μg/ℓ throughout the low concentra-period. Even though influent concentrations were increased by a factor of nearly 20 during the course of the 18-week study, steady-state effluent concentrations were essentially unchanged.

10.7.2 Nitrobenzene

Activated sludge bioreactor studies with nitrobenzene demonstrated that biodegradation effected removals greater than 90% under steady-state conditions. The influent concentration in those studies was maintained in the 90 to 130 μg/ℓ range, and under steady-state operating conditions the effluent concentration varied between 2 and 5 μg/ℓ. This study was designed to evaluate the effect of nitrobenzene concentrations ranging from 100 μg/ℓ to nearly 25,000 μg/ℓ on the removal of nitrobenzene and the overall performance of the activated sludge unit as measured by TOC removal.

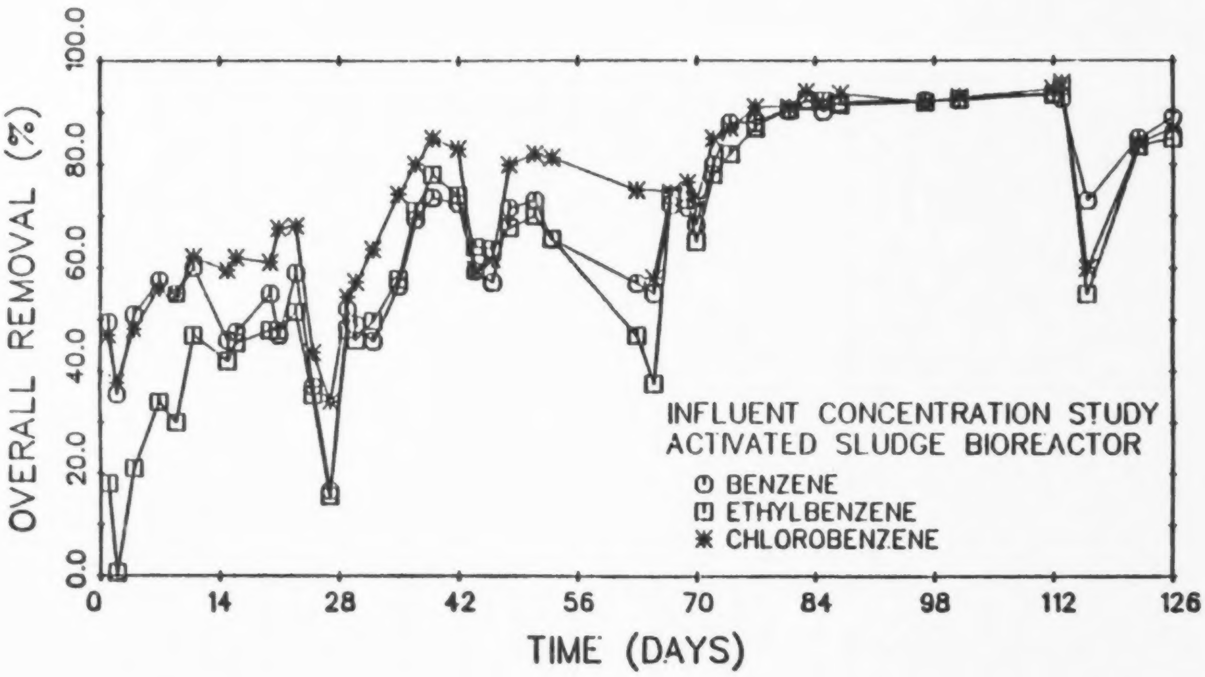


FIGURE 10-125. Comparison of benzene, ethylbenzene, and chlorobenzene overall removals due to biodegradation during periods of low (15 to 30 ug/l) and high (600 to 750 ug/l) influent toxics concentrations to an activated sludge bioreactor.

Influent nitrobenzene concentrations were maintained between 90 and 120 µg/ℓ for the first four weeks to achieve steady-state nitrobenzene removals. Effluent concentrations decreased from approximately 85 µg/ℓ on Day 1 to 3 µg/ℓ on Day 13, and then remained in the 2 to 4 µg/ℓ range. The influent nitrobenzene concentration was increased on Day 30 from 110 to 250 µg/ℓ and remained at that level for approximately one week. There was essentially no change in steady-state effluent nitrobenzene concentration; it remained in the 2 to 4 µg/ℓ concentration range. The influent concentration was further increased to between 500 and 600 µg/ℓ on Day 41 of the bioreactor study. After a small, initial increase, the effluent concentration returned to its previous steady-state level. Table 10-63 lists a summary of results from the nitrobenzene bioreactor study. The most interesting aspect of the data presented in Table 10-63 was the finding that steady-state effluent concentrations were essentially the same even though influent concentrations ranged from 100 to nearly 550 µg/ℓ. The increasing nitrobenzene concentrations had no effect upon overall organics removal as measured by soluble TOC.

Another activated sludge study with nitrobenzene was conducted to evaluate nitrobenzene removal at influent concentrations in the low milligram-per-liter concentration range. The bioreactor initially was acclimated to an influent nitrobenzene concentration of between 90 and 120 µg/ℓ. As in the previously described study, there was an approximate two week acclimation period followed by steady-state effluent concentrations of 3 to 4 µg/ℓ. After two weeks of steady-state nitrobenzene degradation the influent concentration was increased to between 1200 and 1300 µg/ℓ. The effluent nitrobenzene concentration

TABLE 10-63

STEADY-STATE RESULTS FROM NITROBENZENE ACTIVATED SLUDGE STUDY WITH INCREASING INFLUENT CONCENTRATIONS

Influent (µg/ℓ)	Effluent (µg/ℓ)	Removal (%)
116	2.8	98
265	2.4	99
541	3.2	>99

initially rose from 3 to nearly 600 μg/ℓ as a result of the increase in influent concentration from 100 to over 1200 μg/ℓ. Within a week the effluent concentration had decreased to between 1 and 4 μg/ℓ, the same level that occurred when the influent was 100 μg/ℓ. The bioreactor was operated for approximately two weeks with an influent nitrobenzene concentration between 1200 and 1300 μg/ℓ. During that time the steady-state effluent concentration averaged approximately 2.5 μg/ℓ.

The influent nitrobenzene concentration was increased a second time from 1200 μg/ℓ to nearly 25,000 μg/ℓ. The effluent concentration increased from 3 μg/ℓ to approximately 20,000 μg/ℓ and remained at that level for the ten days that 25,000 μg/ℓ of nitrobenzene was added to the influent. Baseline studies indicated that an approximate 20% reduction in aqueous nitrobenzene concentration occurred due to air-stripping in bioreactors without activated sludge. The 20% reduction in aqueous concentration recorded during the 25,000 μg/ℓ nitrobenzene influent concentration caused a reduction in soluble TOC removal from approximately 85% to 40% as effluent TOC concentrations rose from 15 mg/ℓ to nearly 60 mg/ℓ. The high influent nitrobenzene concentration apparently had an inhibitory effect on the microbial activity in the activated sludge that resulted in a reduction in the microorganisms' ability to degrade the organic compounds comprising the synthetic wastewater. A batch TOC degradation study was conducted to measure the effect of the nitrobenzene on the TOC biodegradation rate coefficient. Results of the study given in Figure 10-126 and summarized by Table 10-64 confirmed that the high nitrobenzene concentration effected a reduction in the TOC biodegradation rate coefficient.

Following the 10 day 25,000 μg/ℓ influent concentration operating period the influent concentration was reduced to its original level of approximately 100 μg/ℓ. Within two weeks nitrobenzene removal returned to the 97-98% range as the effluent concentration dropped to between 2 and 4 μg/ℓ. The TOC removal also returned to its previous steady-state level of nearly 85%.

The inhibitory effect caused by the 25,000 μg/ℓ influent concentration was only temporary. It is possible that the activated sludge would have eventually acclimated to the high influent nitrobenzene concentration. Gomolka and Gomolka (59) reported that activated sludge acclimated to nitrobenzene influent concentrations up to 400 mg/ℓ. Only at the highest concentration evaluated, 400 mg/ℓ, did they find an inhibitory effect on the biodegradation of overall organics. The purpose of this study was: 1) to measure nitrobenzene degradation at the microgram-per-liter concentrations likely to be in municipal wastewater, and 2) to evaluate the effect of sudden increases in influent concentration representing a spike loading situation that would be of short duration. The results suggest that no adverse affect in steady-state removal occurred up to influent concentrations of 1200 to 1300μg/ℓ. A steady-state effluent concentration of between 2 and 4 μg/ℓ was recorded for influent concentrations ranging from 100 to 1300 μg/ℓ. An almost complete inhibition in nitrobenzene removal occurred at an

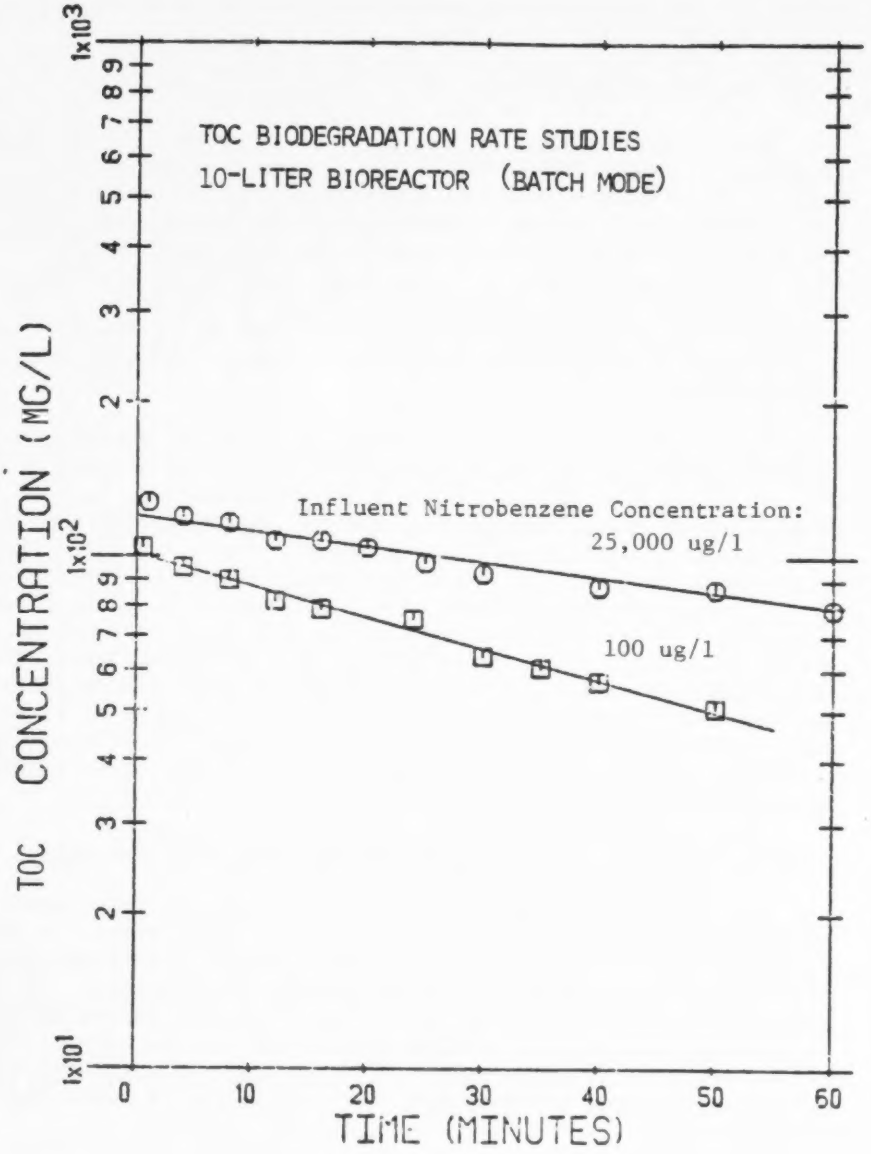


FIGURE 10-126. Effect of a 25,000 ug/l influent nitrobenzene concentration on activated sludge degradation of synthetic wastewater soluble TOC. (TOC degradation rate studies conducted in the 10-liter bioreactor being used for the nitrobenzene activated sludge study.)

influent concentration of 25 mg/ℓ. There was no sign of microbial reacclimation after 10 days of operation at the 25 mg/ℓ level. Once the influent concentration decreased to approximately 100 µg/ℓ the removal of nitrobenzene immediately increased, reaching steady-state levels of 98% within two weeks.

10.8. TRANSIENT LOADING STUDIES

The results presented thus far were obtained from bioreactors receiving a continuous input of toxic organic compounds in the influent flows. While such steady-state loadings were necessary for quantifying the behavior of individual compounds in activated sludge systems, they may not be representative of actual treatment conditions. Rather it is more likely that trace organic priority pollutants are present in influents on a transient basis. An important question is how such transient loading conditions affect the removal of volatile and non-volatile biodegradable compounds for which distinct acclimation periods exist.

The removal of trace toxic organic compounds under transient loading conditions was studied using the 10-liter bioreactors operated in continuous flow modes. Three volatile compounds, benzene, ethylbenzene, and chlorobenzene, and one non-volatile compound, nitrobenzene, were chosen for the study. The three volatile compounds were added simultaneously to an activated sludge bioreactor operated with a 6-day solids retention time. A transient loading study with nitrobenzene was studied in a separate unit also operated at a 6-day solids retention time. Transient loading conditions were obtained by operating the bioreactors on a cycle of two days during which the test organic solutes were added to the influents followed by three to six days during which time the toxic organic compounds were not added to the activated sludge units. All other bioreactor operating conditions were maintained constant.

10.8.1. Benzene, Ethylbenzene, and Chlorobenzene Results

The activated sludge bioreactor receiving benzene, ethylbenzene, and chlorobenzene was operated for a total of 18 weeks. A mean solids retention time and hydraulic residence time of 6 days and 5.5 hours, respectively, were used during the study. The influent TOC ranged between 90 and 120 µg/ℓ and the influent concentrations of the individual toxic organic compounds were maintained between 100 and 150 µg/ℓ. Table 10-65 summarizes five operating periods, with respect to toxics addition to the influent, into which the 18 weeks can be divided.

Influent, effluent, and off-gas concentrations and fractional recoveries, N/N_0, of benzene, ethylbenzene, and chlorobenzene measured during the 18 week transient loading study have been plotted in Figures 10-127, 10-128, and 10-129, respectively. Dashed lines indicate periods of transient toxics loadings while solid lines represent operating periods during which time the toxics were added continuously to the influent. Day 0 represents the initiation of the toxics addition to the

TABLE 10-64

EFFECT OF INFLUENT NITROBENZENE CONCENTRATION ON SOLUBLE TOC REMOVAL

Influent Nitrobenzene Concentration (μg/ℓ)	TOC Biodegradation Rate Coefficient (min^{-1})+
100	0.015
25000	0.007

+ From Figure 10-126

TABLE 10-65

BIOREACTOR OPERATING PERIODS WITH RESPECT TO TOXICS ADDITION DURING THE TRANSIENT LOADING ACTIVATED SLUDGE STUDY

	Time Period	Length (days)	Bioreactor Operating Conditions
1.	Days 0-56	56	Toxics added on a cycle of 2 days present in influent followed by 3 days not present
2.	Days 57-65	9	Toxics added continuously
3.	Days 66-74	9	Toxics not present for 6 days then added for 2 days
4.	Days 75-93	19	Toxics not present in influent
5.	Days 94-125	32	Toxics added on a cycle of 2 days present in influent followed by 6 days not present

TABLE 10-66

COMPARISON OF OVERALL REMOVALS AND BIODEGRADATION RATE COEFFICIENTS MEASURED ON DAY 1 AND DAYS 52-53 OF THE TRANSIENT LOADING STUDY

Compound	Overall Removal (%)$^{+}$ Day 1	Overall Removal (%)$^{+}$ Days 52-53	Biodegradation^{++} Rate Coefficient(min^{-1}) Day 1	Biodegradation^{++} Rate Coefficient(min^{-1}) Days 52-53
Benzene	39	88	0.05	0.48
Ethylbenzene	17	77	0.02	0.26
Chlorobenzene	27	85	0.02	0.26

+ Overall Removal = $100x(1-N/N_0)$

++ Calculated by Equation 10-9

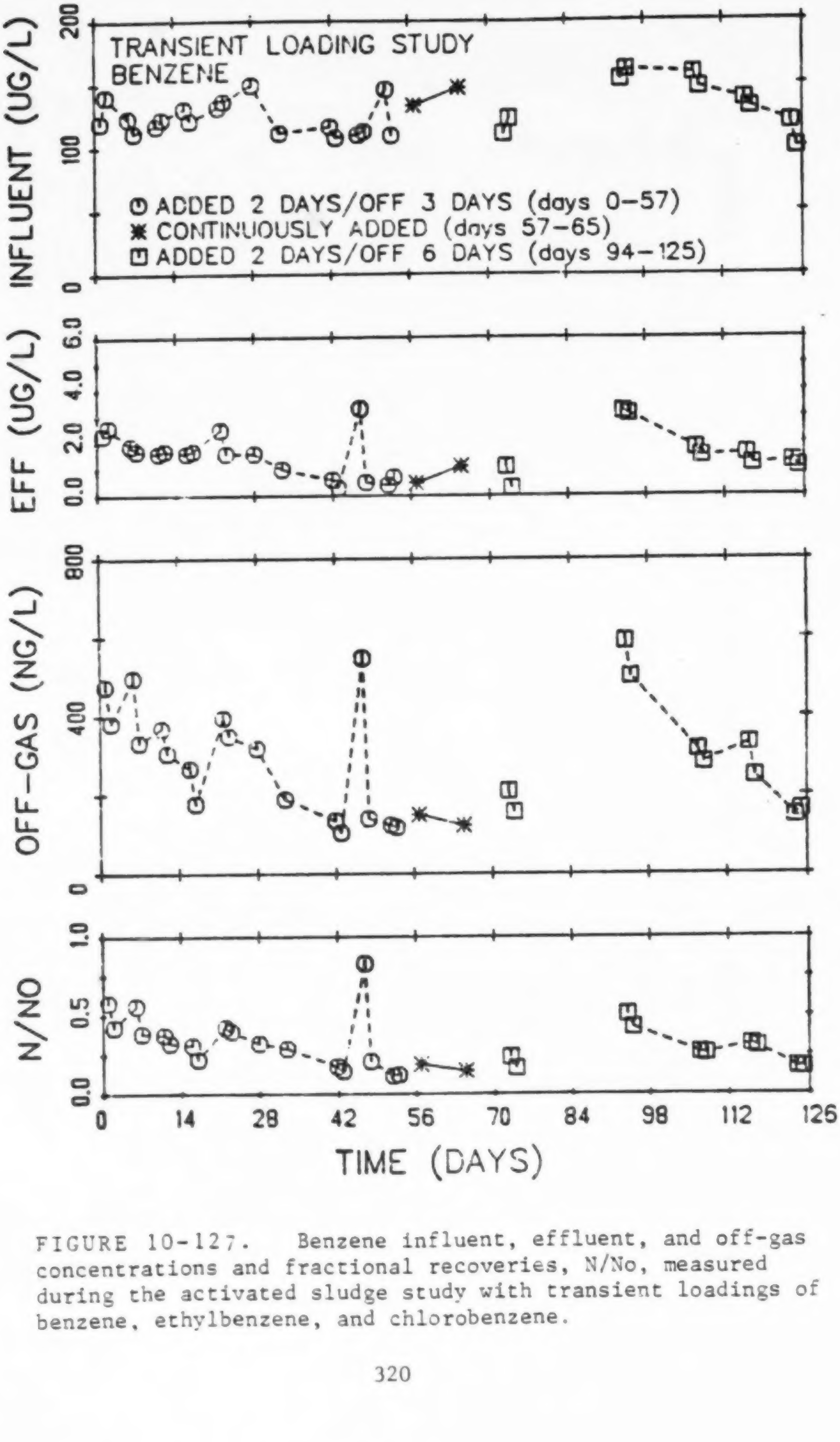


FIGURE 10-127. Benzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the activated sludge study with transient loadings of benzene, ethylbenzene, and chlorobenzene.

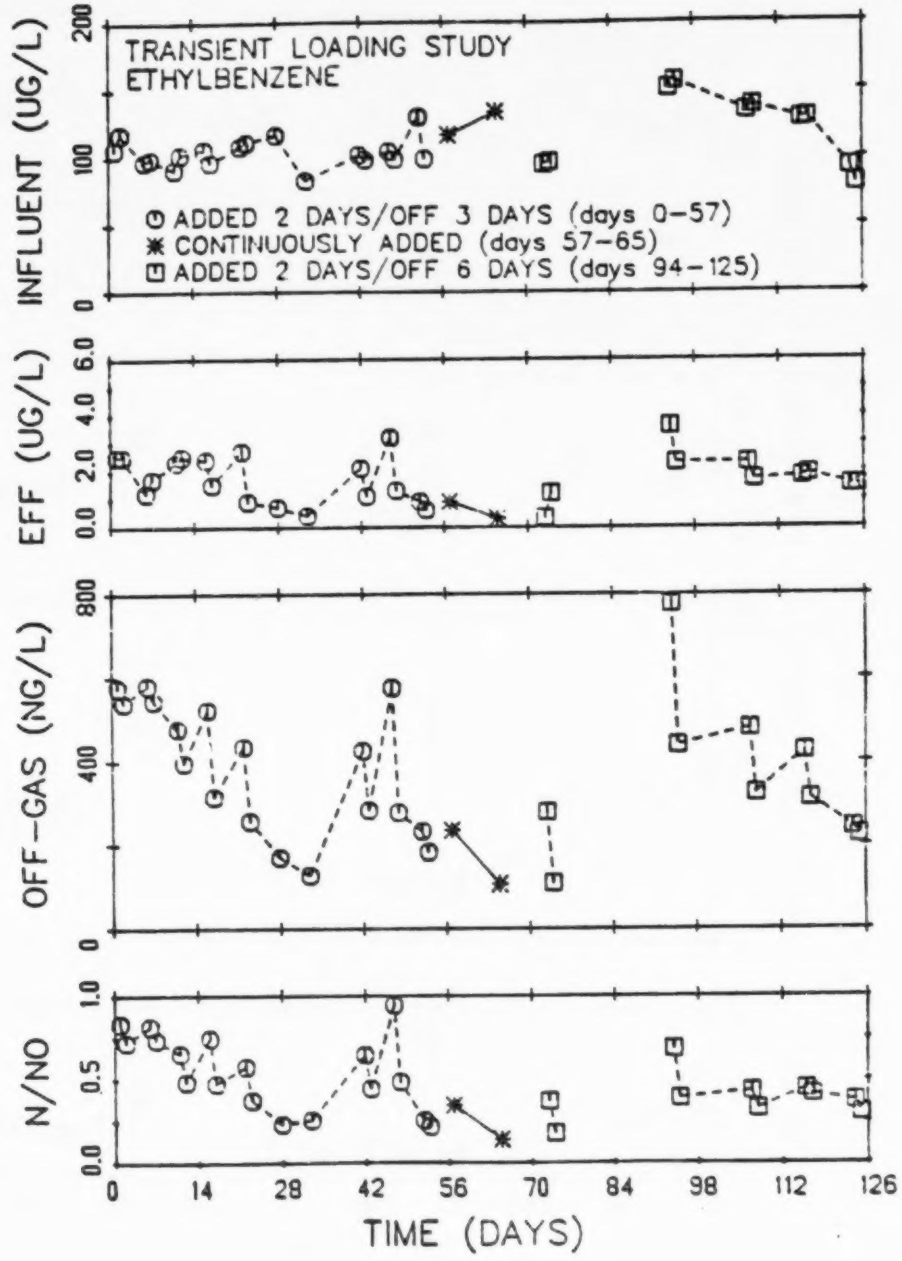


FIGURE 10-128. Ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the activated sludge study with transient loadings of benzene, ethylbenzene, and chlorobenzene.

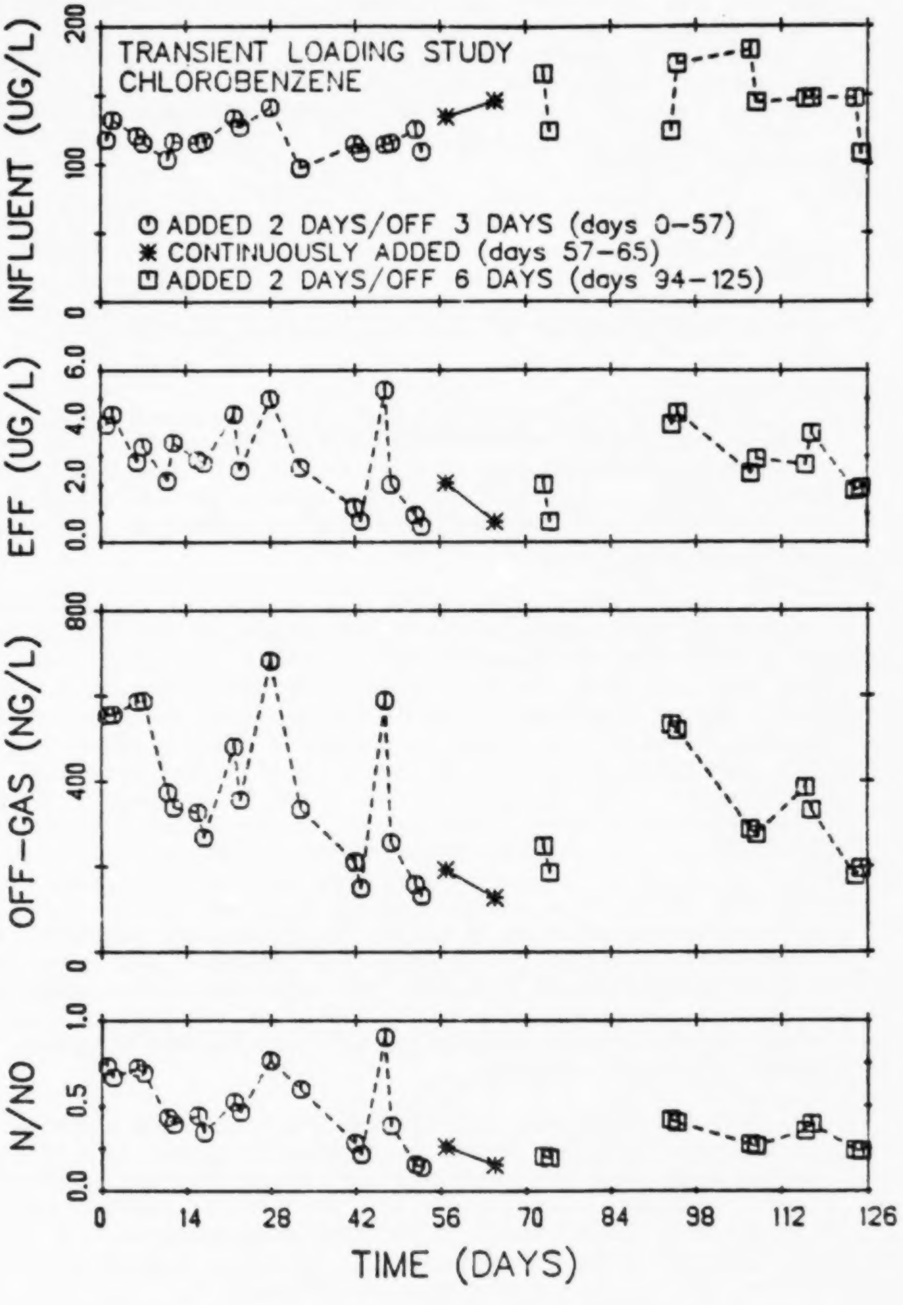


FIGURE 10-129. Chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during the activated sludge study with transient loadings of of benzene, ethylbenzene, and chlorobenzene.

influent. Prior to the addition of the three test compounds to the influent the bioreactor was operated for nearly three weeks to acclimate the microorganisms to the synthetic wastewater. Activated sludge used to seed the bioreactor was obtained from the Ann Arbor wastewater treatment facility. The addition of the three organic compounds on Day 0 had no observable effect on bioreactor performance as measured by traditional operating parameters such as TOC removal, MLSS, and effluent suspended solids.

The results presented by Figures 10-127, 10-128, and 10-129, indicated that the overall removal of each compound due to biodegradation was characterized by an acclimation phase extending from Day 0 to approximately Day 52. As shown by Table 10-66, a significant increase in the overall removal of each compound occurred between Day 1 and Day 52.

In general the removal of benzene due to biodegradation was the largest followed by chlorobenzene and ethylbenzene in decreasing order, as shown by the comparison of results for all three compounds between Days 0 and 70 in Figure 10-130. The same order was observed in single and multi-solute activated sludge studies conducted with continuous toxics loadings.

A sudden increased recovery of each compound on Day 46 was observed to coincide with a drop in the mixed liquor pH from approximately 7.2 to 6.2. The pH decreased due to tubing fatigue in the feed pump supplying tap water containing $NaHCO_3$ buffer to the influent flow. Within a maximum of twelve hours the pH had been adjusted to its original level of 7.2. Samples collected one day later, Day 47, showed that both effluent and off-gas concentrations had decreased significantly from values recorded on Day 46 as a result of increased biodegradation of each compound. While the pH-induced upset episode effected significant reductions in the biodegradation of the three toxic organic compounds, the effect was only temporary. Within 24 to 36 hours after the pH had been adjusted to its original level, the system had returned to its previous levels of biodegradative removal. Similar results were observed for benzene, ethylbenzene, and chlorobenzene in other activated sludge studies. The magnitude of the reductions in biodegradation were larger during the transient loading study, but the length of the effects was similar to that observed in other activated sludge bioreactor studies.

Influent, effluent, and off-gas concentrations and N/N_0 values for benzene, ethylbenzene, and chlorobenzene from Days 0-74 of the transient loading study have been compared with results from steady-state loading studies in Figures 10-131, 10-132 , and 10-133, respectively. In each case the N/N_0 values measured on Day 1 were approximately the same for each compound in both continuous and transient loading studies indicating that initial biodegradation rate coefficients were similar. The results for benzene in Figure 10-131 show that removal of benzene by activated sludge in the steady-state and transient studies was approximately the same with the exception of the pH-induced upset episode on day 46.

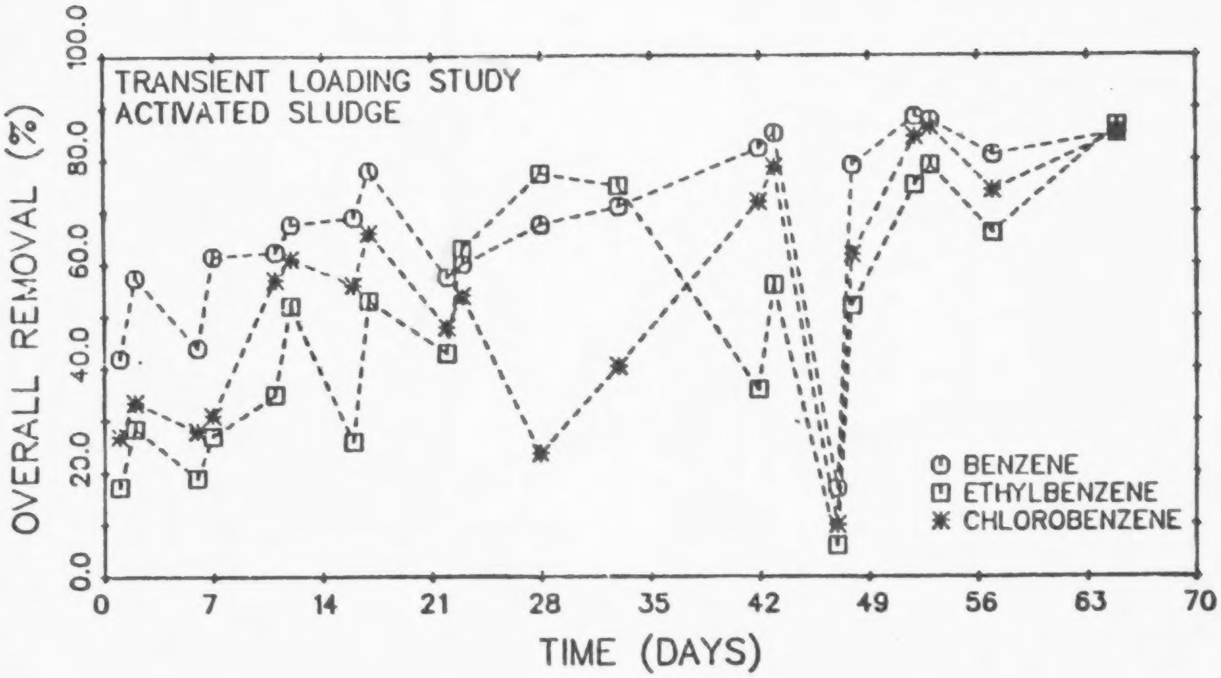


FIGURE 10-130. Benzene, ethylbenzene, and chlorobenzene overall removals due to biodegradation during the initial 66 days of the activated sludge study with transient toxics loadings. (Toxics added to the influent for 2 days and then omitted for 3 days during days 0-56.)

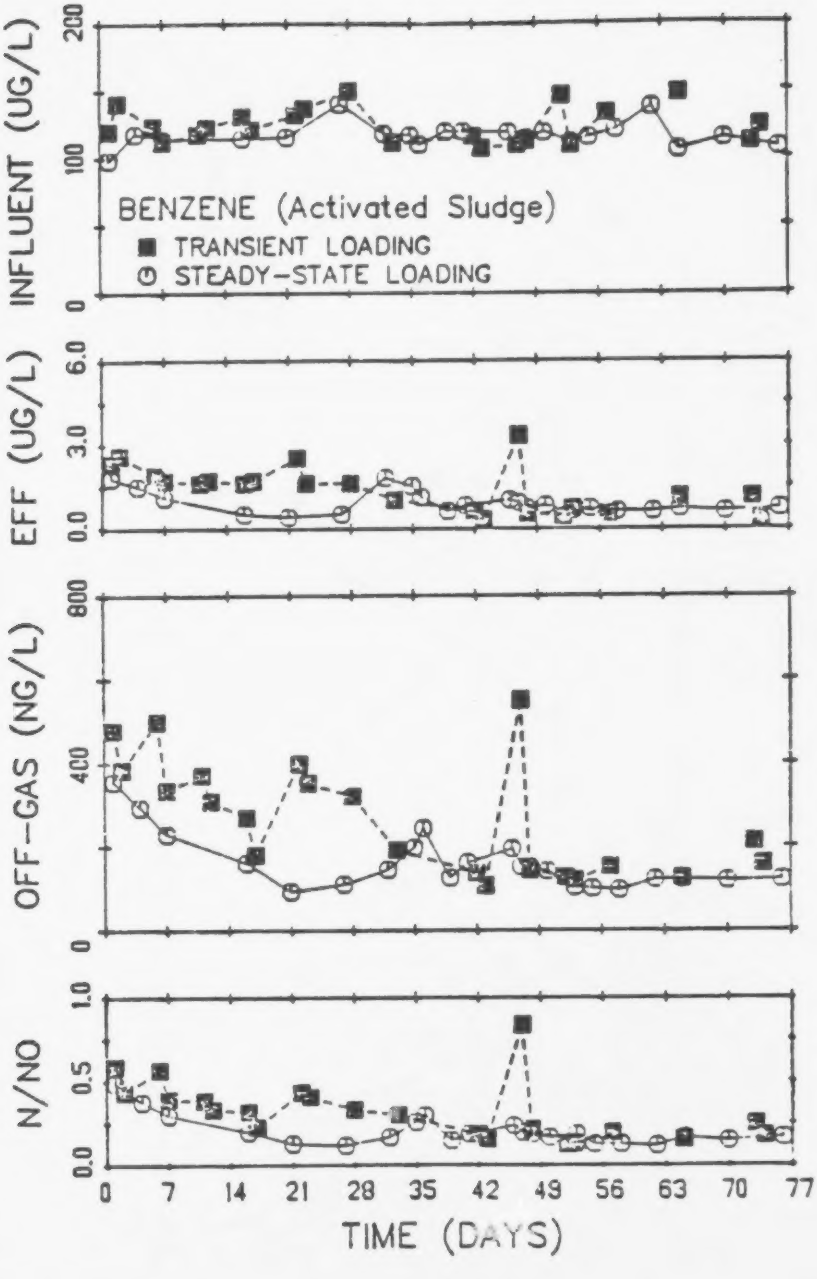


FIGURE 10-131. Comparison of benzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during activated sludge studies with transient (2 days added/ 3 days omitted for days 0-56) and steady-state toxics loadings.

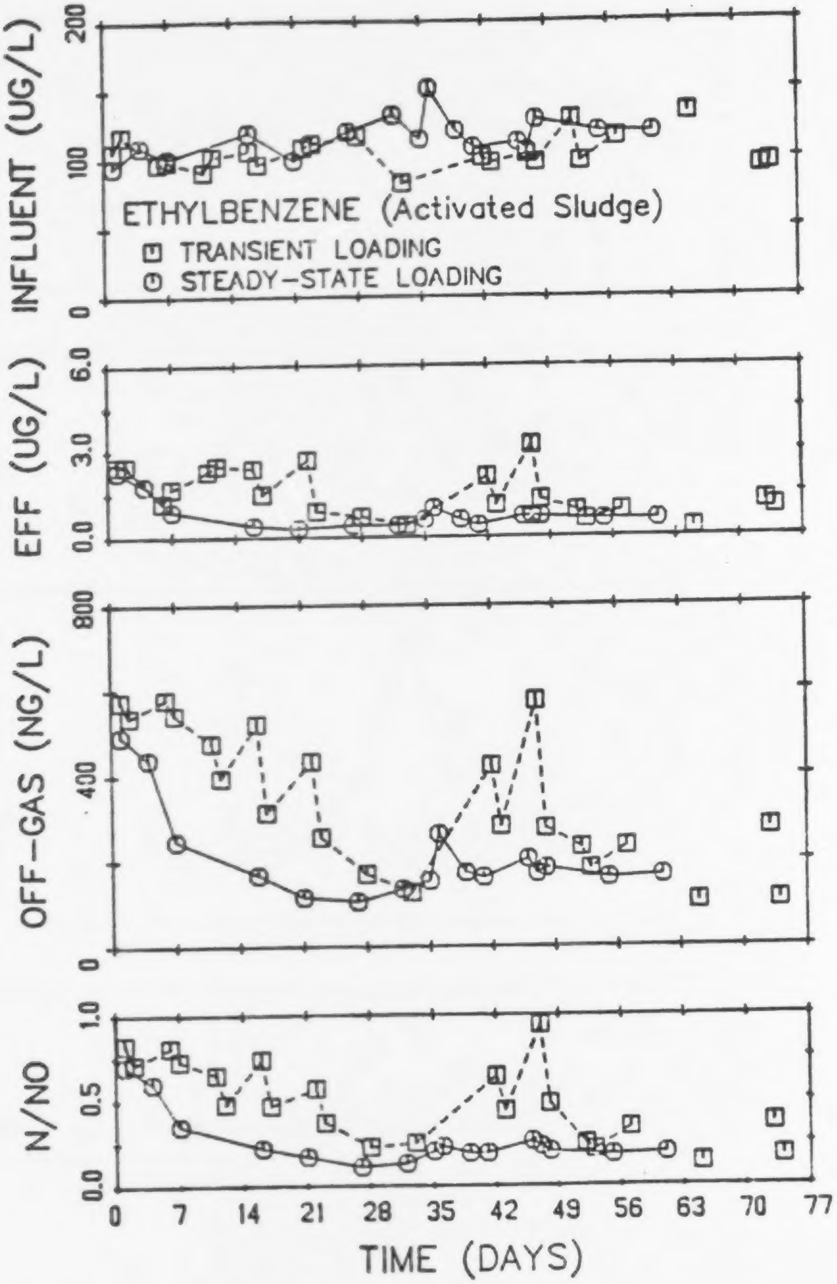


FIGURE 10-132. Comparison of ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during activated sludge studies with transient (2 days added/3 days omitted for days 0-56) and steady-state toxics loadings.

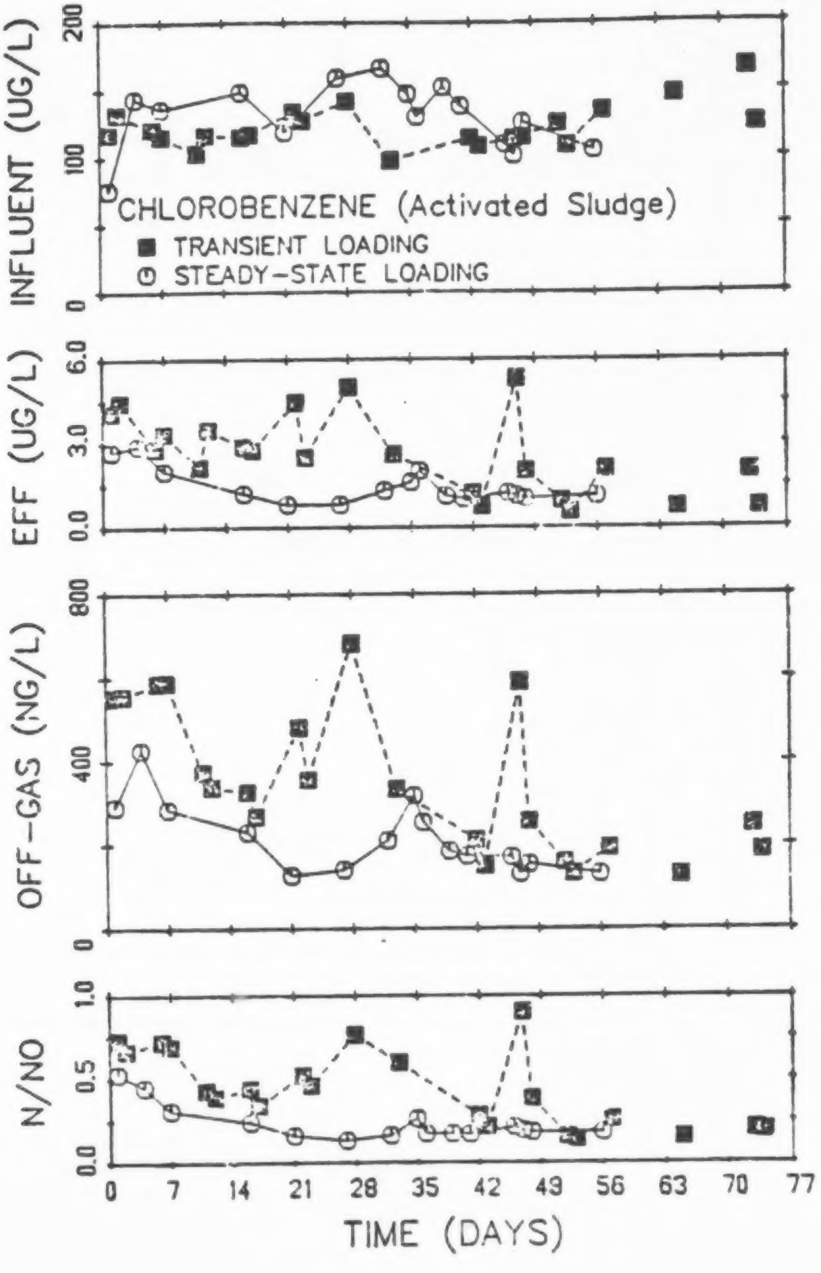


FIGURE 10-133. Comparison of chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during activated sludge studies with transient (2 days added/3 days omitted for days 0-56) and steady-state toxics loadings.

difference in effluent or off-gas concentrations between the two studies after Day 35. During the acclimation period, however, the overall removal of benzene in the steady-state loading bioreactor was slightly greater as indicated by the smaller N/N_0 values.

The comparison of results for ethylbenzene under steady-state and transient loading conditions in Figure 10-132 indicates that the removal of ethylbenzene during the acclimation period, Days 0-28, was slightly better in the bioreactor with the steady-state loadings. The length of the acclimation periods in both studies was between 21 and 28 days. With the exception of the results from the transient study collected between Days 42 and 49, the overall removals after acclimation were approximately the same. The transient loading bioreactor experienced an upset between Days 42 and 49, therefore the data collected during that period was likely to be unrepresentative of the removals under steady-state bioreactor conditions.

The comparison of results for chlorobenzene from steady-state and transient loading studies, plotted in Figure 10-133, indicated greater overall removal due to biodegradation occurred during the acclimation phase of the steady-state loading reactor. The results after Day 49 were approximately the same for the two loading studies.

While exact effluent and off-gas concentrations and overall toxic removals observed during acclimation periods were found to vary from study to study, an interesting trend was observed during the transient study. Two reactor samples were generally collected during the period when toxics were added to the influent, the first between 18 and 24 hours and the second between 36 and 48 hours after the toxics addition was begun. The amount of each compound biodegraded by the activated sludge was larger on the second day than on the first day of each toxics addition period. The greater amount of degradation on the second day is evidenced in the N/N_0 values for the second data point in each pair of points representing samples collected during the toxics addition periods. The removal of each compound during the 2-day period when toxics were added was more thoroughly investigated on two occasions by sampling the bioreactor every four to eight hours during this period.

The first detailed sampling was conducted from Days 42 to 43, and the results for benzene, ethylbenzene, and chlorobenzene are given by Figure 10-134. The overall removal of each compound due to biodegradation increased during the sampling period as shown by the decreasing trend in fractional recoveries, N/N_0. The order of removal was the same as observed to occur throughout the 126 days of the transient study:

benzene > chlorobenzene > ethylbenzene

Table 10-67 provides a comparison of measured overall removals and calculated first-order biodegradation rate coefficients at the beginning and end of the 38-hour study.

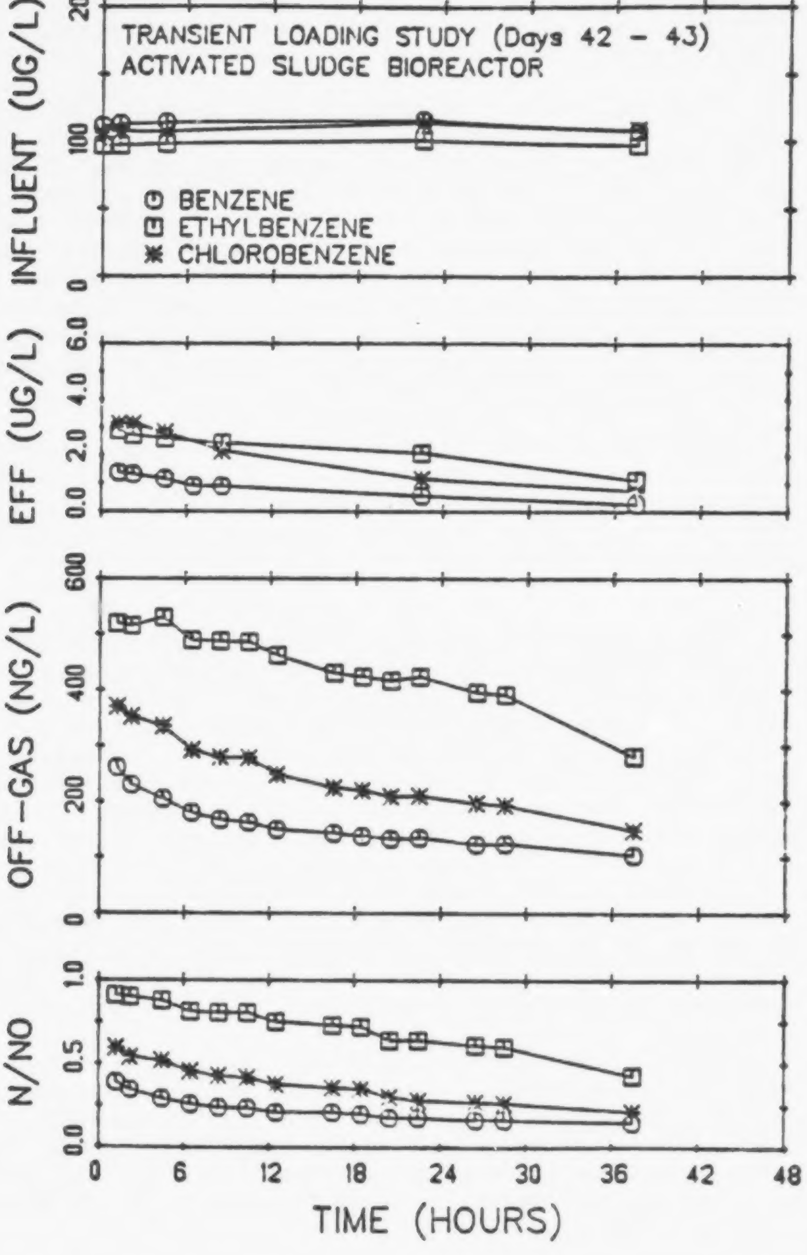


FIGURE 10-134. Changes in benzene, ethylbenzene, and chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, due to increased microbial degradation during the 2-day toxics addition period, Days 42 to 43.

The second sampling period was conducted on Day 57; influent, effluent, and off-gas concentrations and N/N_0 values are given by Figure 10-135. The same relative order of removals was observed:

benzene > chlorobenzene > ehtylbenzene

Overall removals of each compound increased during the 24 hours sampling period with the largest increase occurring for ethylbenzene. A comparison of overall removals and biodegradation rate coefficients measured 2 and 24 hours after toxics addition to the influent was begun on Day 57 is given in Table 10-68.

TABLE 10-67

COMPARISON OF OVERALL REMOVAL AND BIODEGRADATION RATE COEFFICIENTS AT 2 AND 38 HOURS DURING THE TOXICS ADDITION PERIOD DAYS 42-43

Compound	Overall Removal(%) 2 hr.	Overall Removal(%) 38 hr.	Biodegradation Rate Coefficient(min^{-1}) 2 hr.	Biodegradation Rate Coefficient(min^{-1}) 38 hr.
Benzene	61	85	0.13	0.44
Ethylbenzene	9	57	0.01	0.12
Chlorobenzene	41	79	0.04	0.20

TABLE 10-68

COMPARISON OF OVERALL REMOVAL AND BIODEGRADATION RATE COEFFICIENTS AT 2 AND 24 HOURS DURING THE TOXICS ADDITION PERIOD OF DAY 57

Compound	Overall Removal(%) 2 hr.	Overall Removal(%) 24 hr.	Biodegradation Rate Coefficient(min^{-1}) 2 hr.	Biodegradation Rate Coefficient(min^{-1}) 24 hr.
Benzene	75	81	0.22	0.33
Ethylbenzene	20	66	0.02	0.19
Chlorobenzene	62	74	0.08	0.15

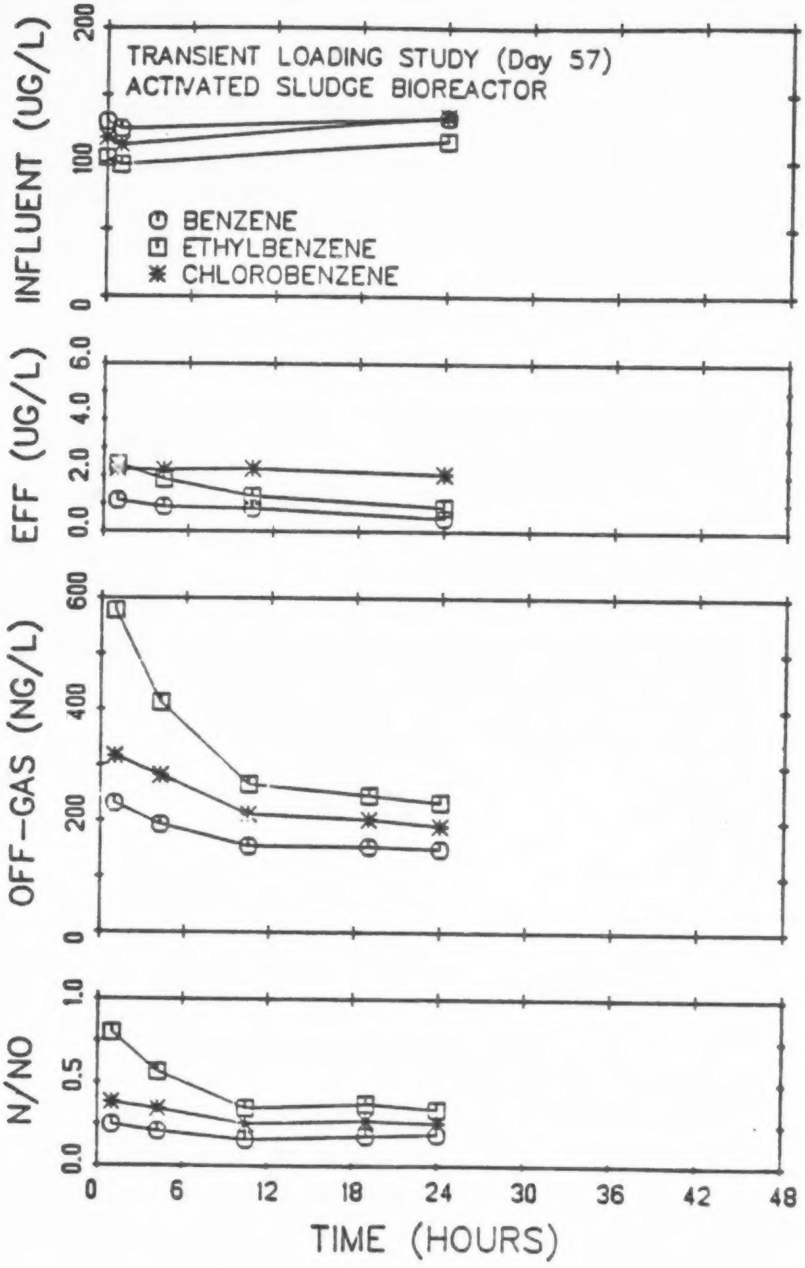


FIGURE 10-135. Changes in benzene, ethylbenzene, and chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, due to increased microbial degradation during the 1-day toxics addition period, Day 57.

Results for benzene from the two sampling periods, Days 42-43 and Day 57, were nearly identical, as shown by Figure 10-136. Results for chlorobenzene, given by Figure 10-137, indicated that the overall removal decreased slightly faster during the second in-depth sampling period. The data for ethylbenzene given by Figure 10-138 showed that the approach to steady-state biodegradation was significantly more rapid during the study conducted on Day 57, as evidenced by the reductions in N/N_0 values. The results from the two studies indicated that during each two-day period of toxics addition there was an increase in the amount of each compound biodegraded. During the acclimation phase of the study that increase likely continued throughout the two days the toxics were added to the influent. Once the system had fully acclimated to the three compounds overall removals increased during the first 24 hours to their respective steady-state levels.

The significant finding of the in-depth sampling periods was that during transient toxics loading conditions the overall removal of the three compounds went through a short reacclimation phase rather than continuing at the level that existed when toxics addition was discontinued. When fully acclimated this reacclimation phase was short and the system returned to steady-state toxics biodegradation within 24 hours.

After the overall removal of each compound in the transient loading bioreactor reached the approximate steady-state levels observed in previous activated sludge studies, the three organic compounds were added continuously to the influent for 8 days beginning on Day 57. There was an increase in the removals of ethylbenzene, and, to a lesser extent, chlorobenzene, during that time such that by Day 65 approximately 85% of each compound was biodegraded by the activated sludge. No increase in benzene removal occurred.

Following the continuous addition period the toxics were omitted from the influent for 6 days, Days 66 to 72; then added for two days. The 6 day interruption had the most significant impact on ethylbenzene removal causing it to decrease from 85% on Day 65 to 63% on Day 73. After the second day of toxics addition, Day 74, the overall ethylbenzene removal returned to 83%, approximately the same level observed on Day 65. The 6-day interruption had a minimal effect on benzene and chlorobenzene removals. Both compounds experienced only slight reductions in removals on Day 73 and then by Day 74 returned to the approximate levels recorded on Day 65.

In an effort to evaluate the effect of an extended period of toxics interruption on the biodegradative removal of benzene, ethylbenzene, and chlorobenzene toxics addition to the transient loading bioreactor was stopped after the reactor sample on Day 74. When the toxics were added to the influent again 19 days later, Day 93, the overall removals of each compound had decreased significantly. The N/N_0 values measured on Day 94 were approximately the same as measured on Day 1 of the transient loadings study indicating the activated sludge's ability to degrade the toxics had decreased to the level observed at the beginning of the study.

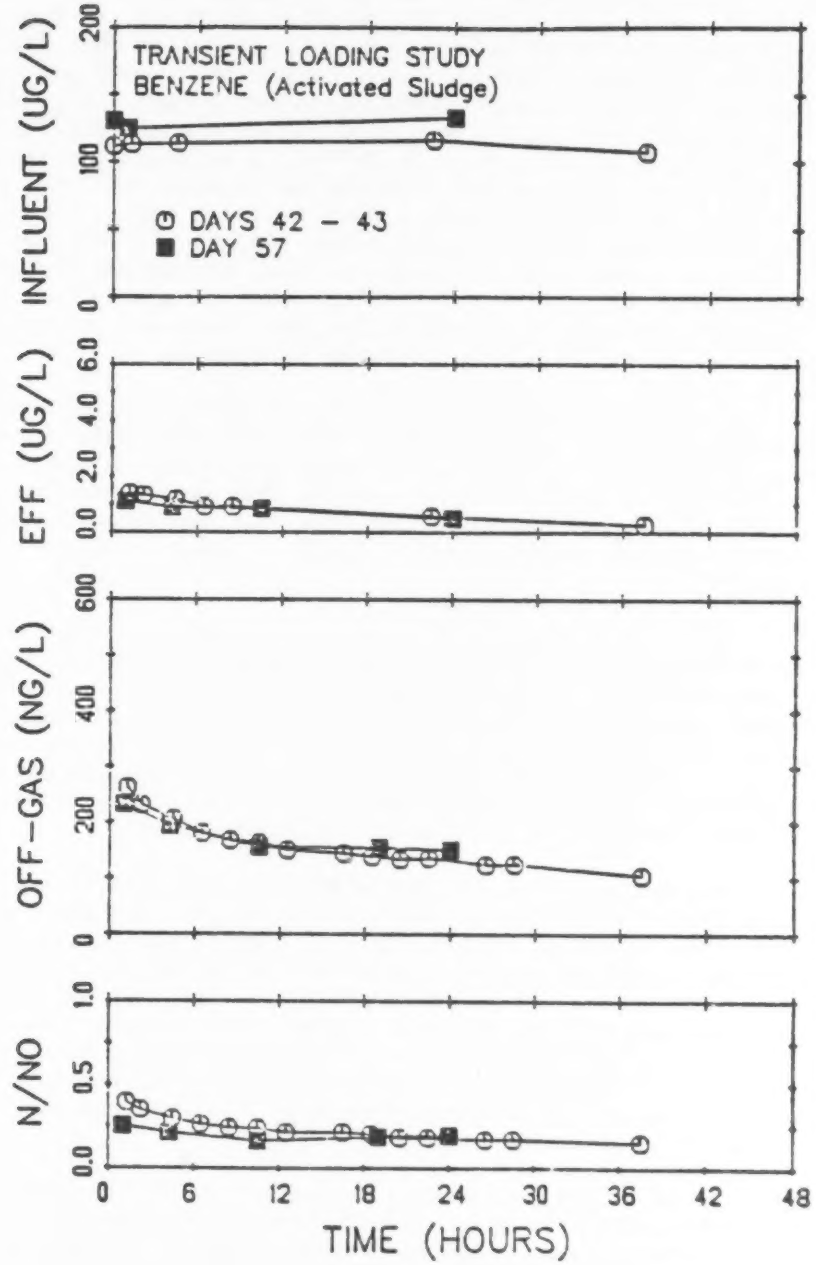


FIGURE 10-136. Comparison of the reductions in benzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during two toxics addition periods.

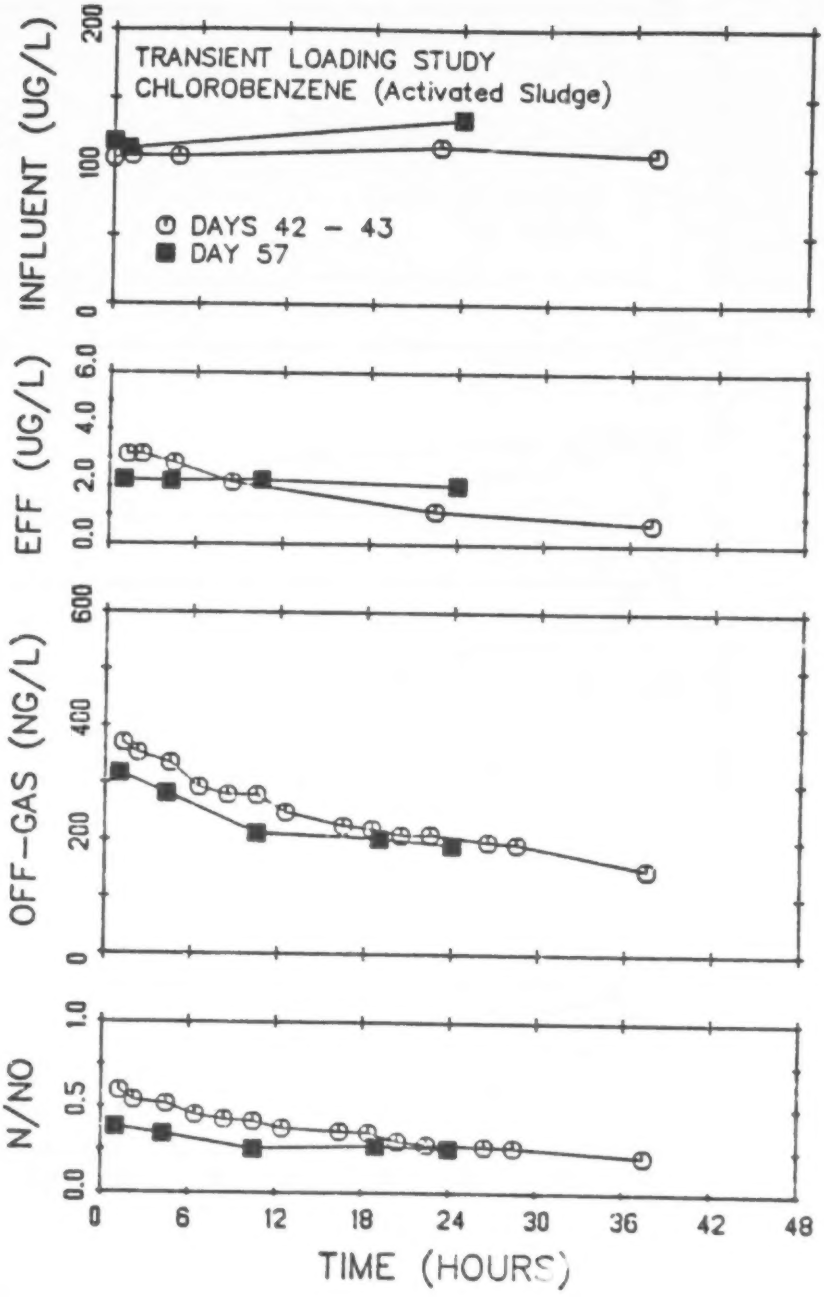


FIGURE 10-137. Comparison of the reductions in chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during two toxics addition periods.

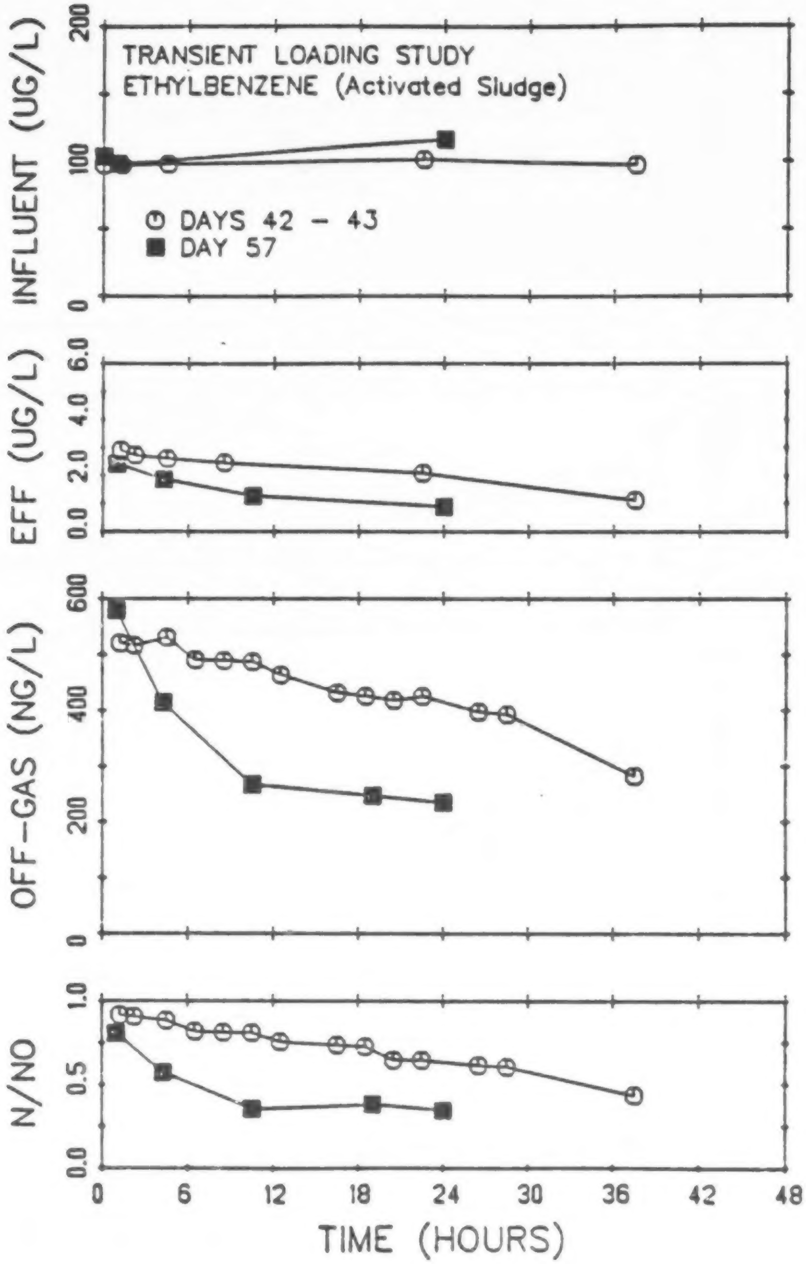


FIGURE 10-138. Comparison of the reductions in ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No, during two toxics addition periods.

Following the 19-day period when toxics were not added to the influent the toxics addition cycle was changed to a two day addition period followed by a six day interruption period. This cycle approximates a situation in which the activated sludge is exposed to the toxic organic compounds for only two days out of the six days comprising one mean solids residence time. Comparisons of the initial acclimation (Days 0-42) and reacclimation periods for benzene, ethylbenzene, and chlorobenzene are given in Figures 10-139, 10-140, and 10-141. The results were approximately the same indicating the longer period without toxics, six days compared with three days, had little impact upon the activated sludge's ability to acclimate to the three organic compounds. Typically the sample collected on the second day of the addition period indicated a greater removal of each compound had occurred than was measured on the first day of that period. As occurred during the first part of the transient toxics loading study, benzene removal was typically the largest, followed by chlorobenzene and ethylbenzene in that order. A comparison of the data for the three compounds is presented by Figure 10-142.

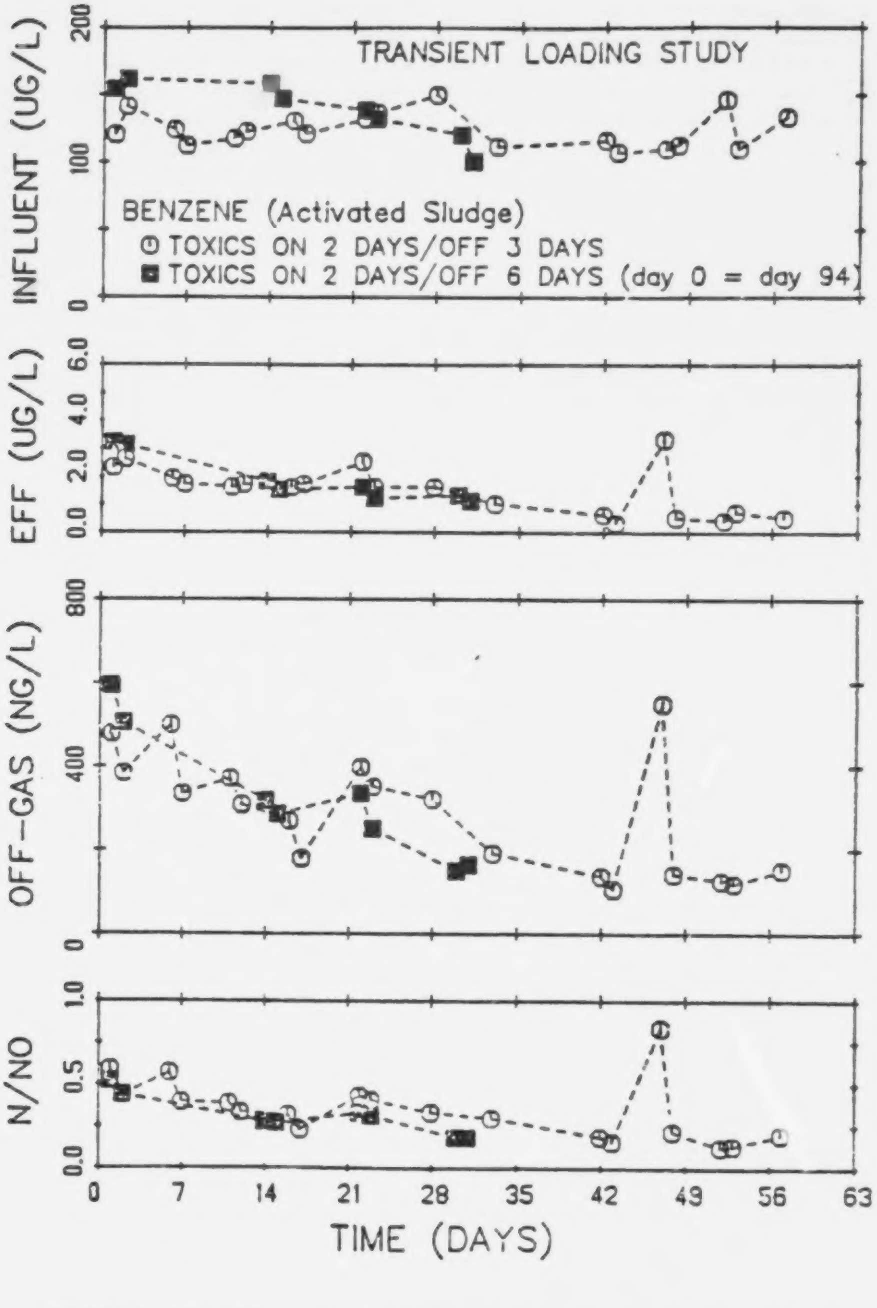


FIGURE 10-139. Comparison of benzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during toxics loading cycles of 2 days added/3 days omitted and 2 days added/6 days omitted.

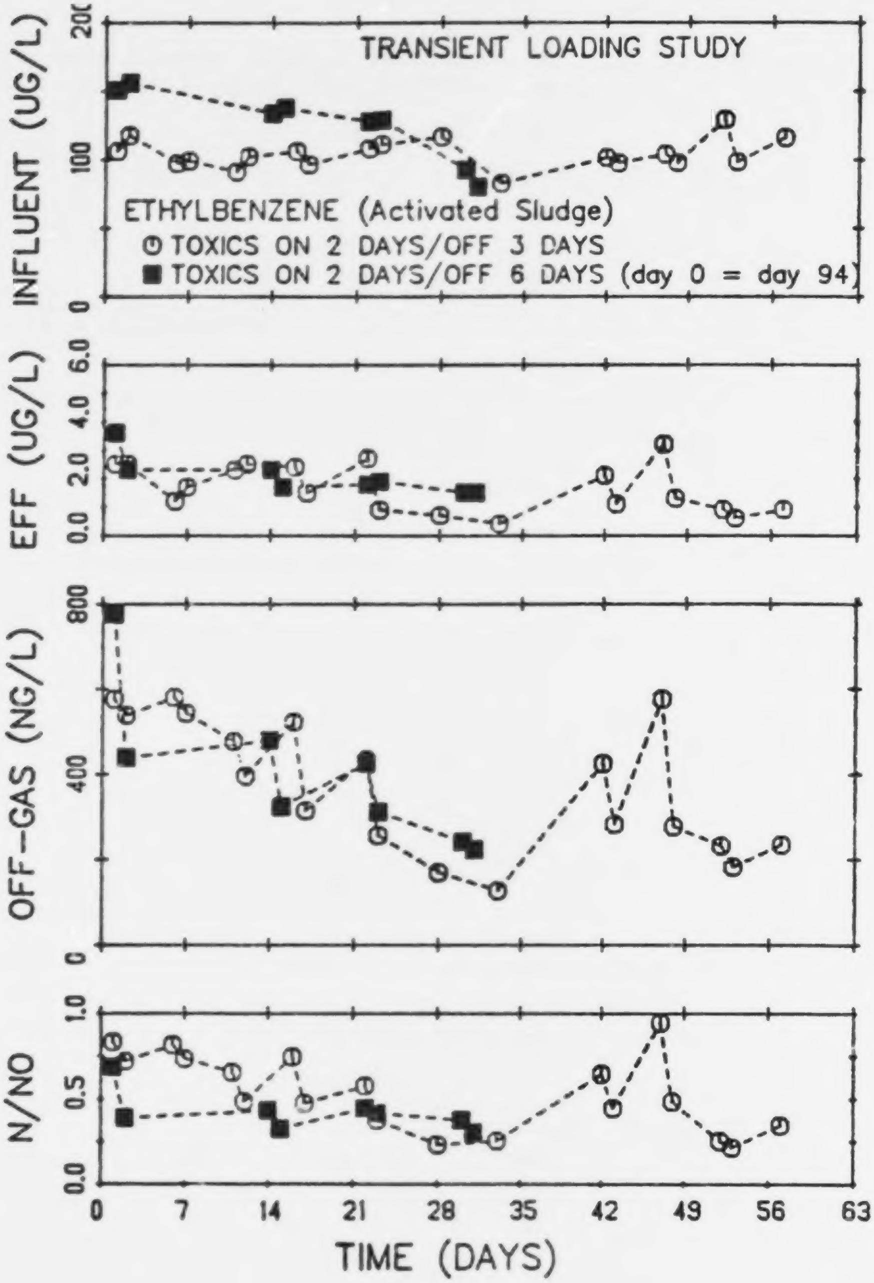


FIGURE 10-140. Comparison of ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during toxics loading cycles of 2 days added/3 days omitted and 2 days added/6 days omitted.

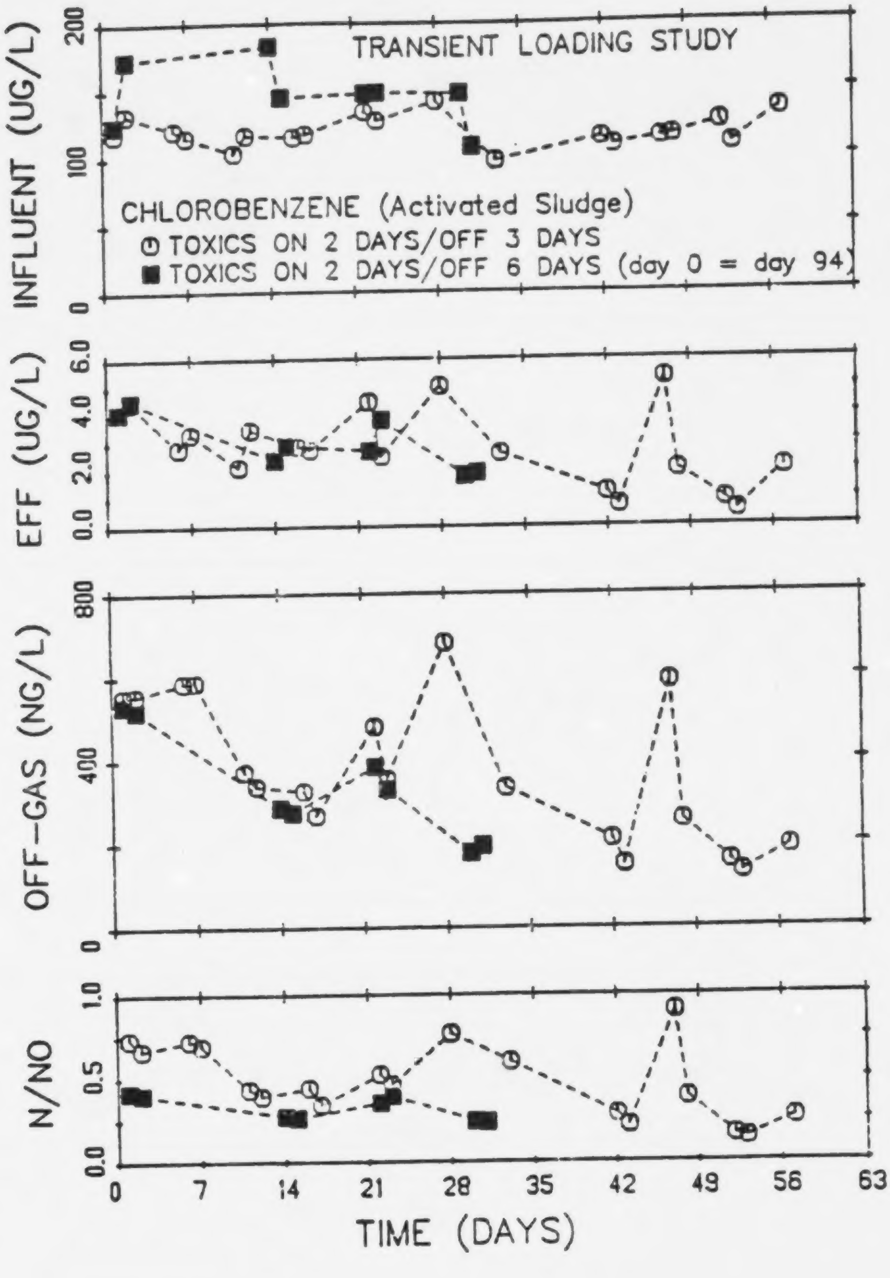


FIGURE 10-141. Comparison of chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during toxics loading cycles of 2 days added/3 days omitted and 2 days added/6 days omitted.

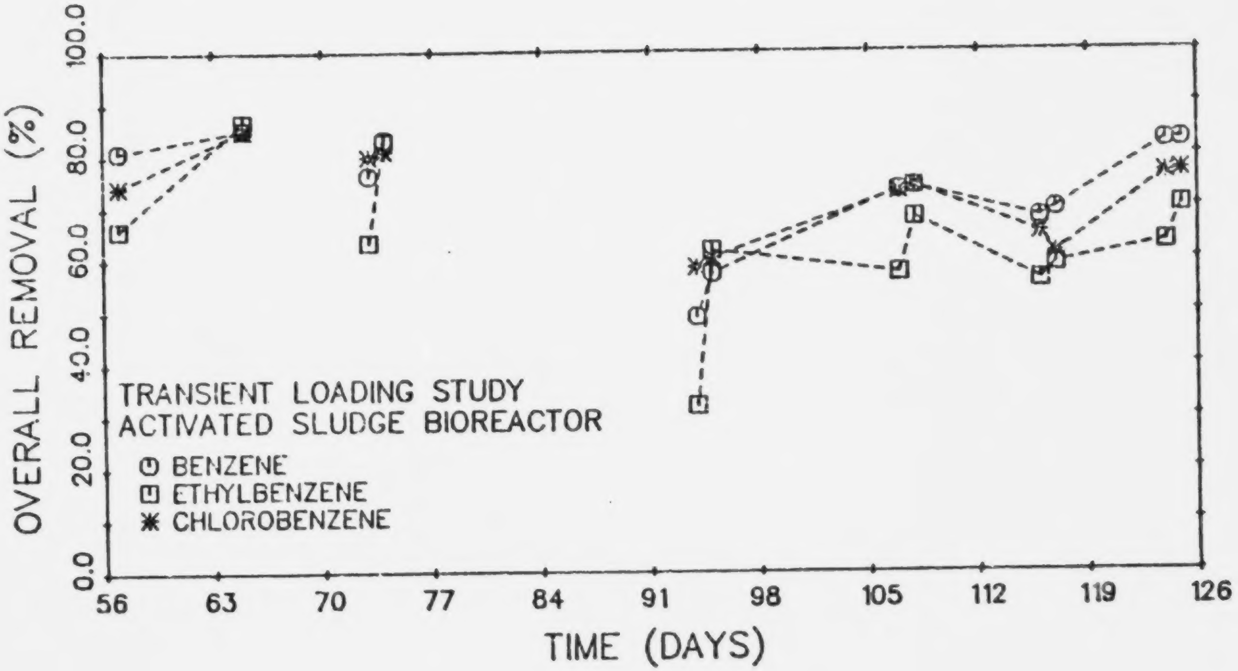


FIGURE 10-142. Comparison of benzene, ethylbenzene, and chlorobenzene overall removals due to biodegradation during the final 70 days of the transient toxics loading activated sludge study.

SECTION 11

RESULTS: INTEGRATED ACTIVATED SLUDGE/CARBON ADSORPTION BIOREACTOR STUDIES

The removal of each toxic organic comound by integrated powdered activated carbon/activated sludge treatment was studied in the 10-liter experimental bioreactors operated in continuous flow modes. Control activated sludge units not receiving powdered activated carbon (PAC) were operated in parallel with the PAC units. Bioreactor operating conditions were similar to those reported for the activated sludge studies in Section 10. The majority of the studies were conducted in bioreactors operated with a 5.5 hour hydraulic retention time and a 6-day solids retention time. Bioreactor influents were composed of the synthetic wastewater detailed in Table 5-3, toxics organic solution, and either slurried PAC or tap water. Additional PAC bioreactor studies with lindane were conducted with primary effluent from the Ann Arbor wastewater treatment facility as the source of influent wastewater.

Results from PAC bioreactor studies presented in Section 11 are divided into four different types of studies:

1. Effect of Influent PAC Dose. Bioreactor studies were conducted with each compound to evaluate the effect of influent PAC dose upon overall removals. These studies typically were conducted in bioreactors receiving only one toxic organic compound.

2. Effect of Solids Retention Time. PAC bioreactor studies were conducted at a constant PAC dose to determine whether the solids retention time affected toxics removals.

3. PAC-Interruption Study. Bioreactor studies were conducted to evaluate the effect of interrupting PAC addition upon the removal of both biodegradable and non-biodegradable toxic organic compounds.

4. Transient Loading Study. The effect of transient toxics loadings on the removal of a combination of toxic organic compounds in a PAC bioreactor was evaluated.

11.1 BIOREACTOR OPERATING CONDITIONS

The removal of toxic organic compounds in integrated powdered activated carbon/activated sludge systems was studied in the 10-liter experimental bioreactors operated in continuous flow modes. Control activated sludge units not receiving PAC were operated in parallel with each PAC unit during the initial phases of the study. During later experiments evaluating the effect of additional PAC influent doses, control bioreactors were not always used to allow more PAC studies to be conducted.

Bioreactor operating conditions were similar to those reported for the activated sludge studies. The majority of the studies were conducted with a 5.5-hour hydraulic retention time and a 6-day solids retention time. Except for a few studies with lindane the synthetic wastewater detailed in Table 5-3 was used. A summary of pertinent bioreactor operating conditions is given in Table 11-1.

11.2 PAC ADSORPTION STUDIES

Equilibrium adsorption studies were conducted to compare the adsorptive capacities of the various adsorbents for each of the toxic organic compounds. Initial isotherm studies were conducted with lindane, 1,2-dichlorobenzene and nitrobenzene to select a principal PAC to be used in the PAC bioreactor studies. The initial isotherms were conducted in various background solutions including deionized-distilled water, bioreactor influent, effluent from a control activated sludge unit, and bioreactor mixed liquor which included mixed liquor suspended solids. Results from these studies have been graphically presented in linearized form in Figures 11-1 through 11-5. The Freundlich isotherm equation was used to model the adsorption of each of the toxic organic compounds. The Freundlich isotherm is described by

$$q_e = K_f \, C_e^{1/n}$$

which can be written in linearized form as

$$\log q_e = \log K_f + (1/n) \log C_e$$

where C_e(μg/ℓ) is the equilibrium solution concentration, q_e(μg/mg) is the amount adsorbed per unit of weight of activated carbon and K_f and $1/n$ are Freundlich isotherm constants.

In general the experimental, high surface area powdered activated carbon, PX-21, exhibited the largest capacity to adsorb lindane and 1,2-dichlorobenzene at a given equilibrium solution concentration. Results obtained with the two commercial powdered activated carbons Hydrodarco C and SA-15 were quite similar. Based upon its similar performance to the other powdered activated carbon and recommended usage by the manufacturer for full-scale PACT® treatment facilities, Hydrodarco C was selected as the principal PAC to be used in the PAC-addition to activated sludge studies.

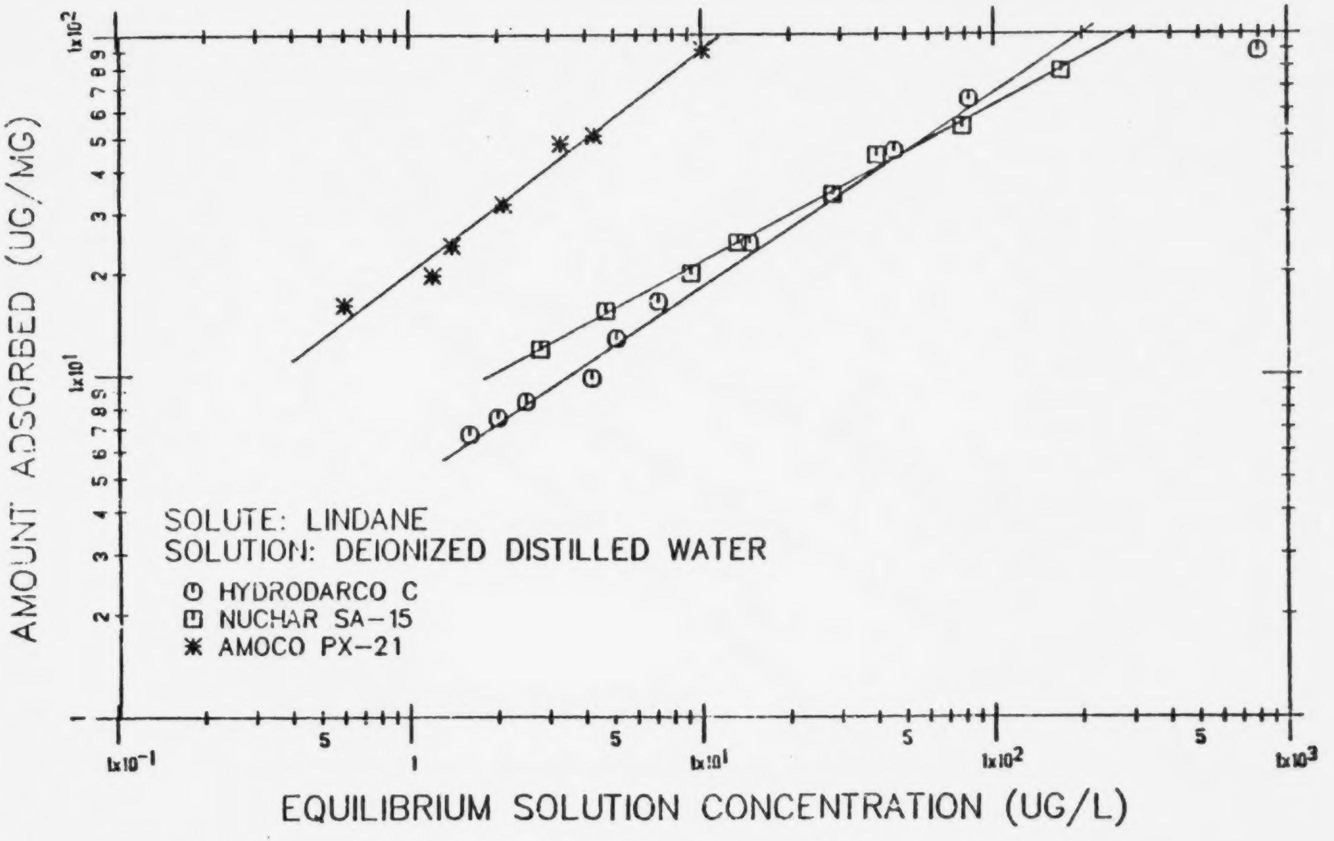


FIGURE 11-1. Experimental data and best-fit lines describing the adsorption of lindane by three powdered activated carbons: Hydrodarco C, SA-15, and PX-21.

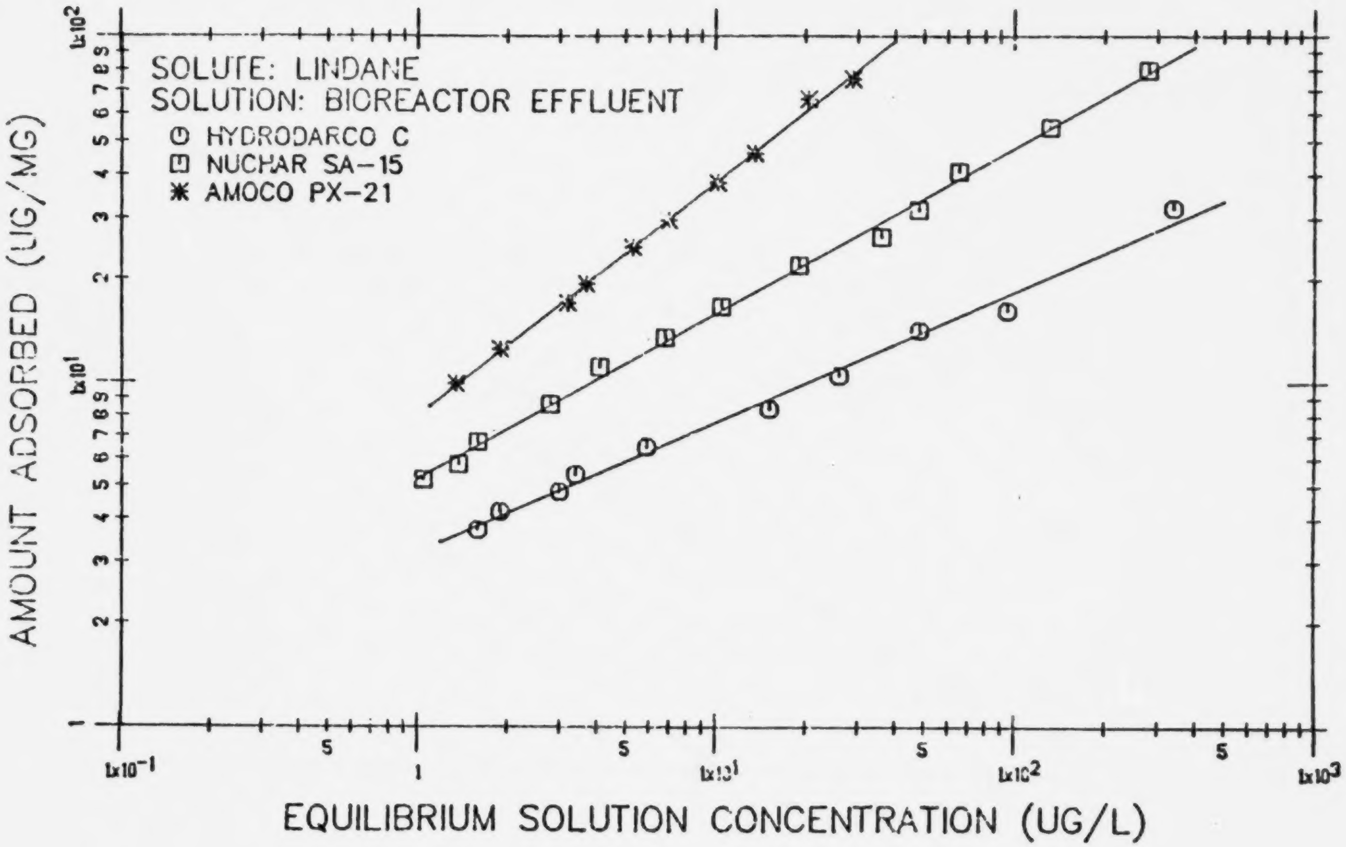


FIGURE 11-2. Experimental data and best-fit lines describing the adsorption of lindane from activated sludge bioreactor effluent by three powdered activated carbons: Hydrodarco C, SA-15, and PX-21.

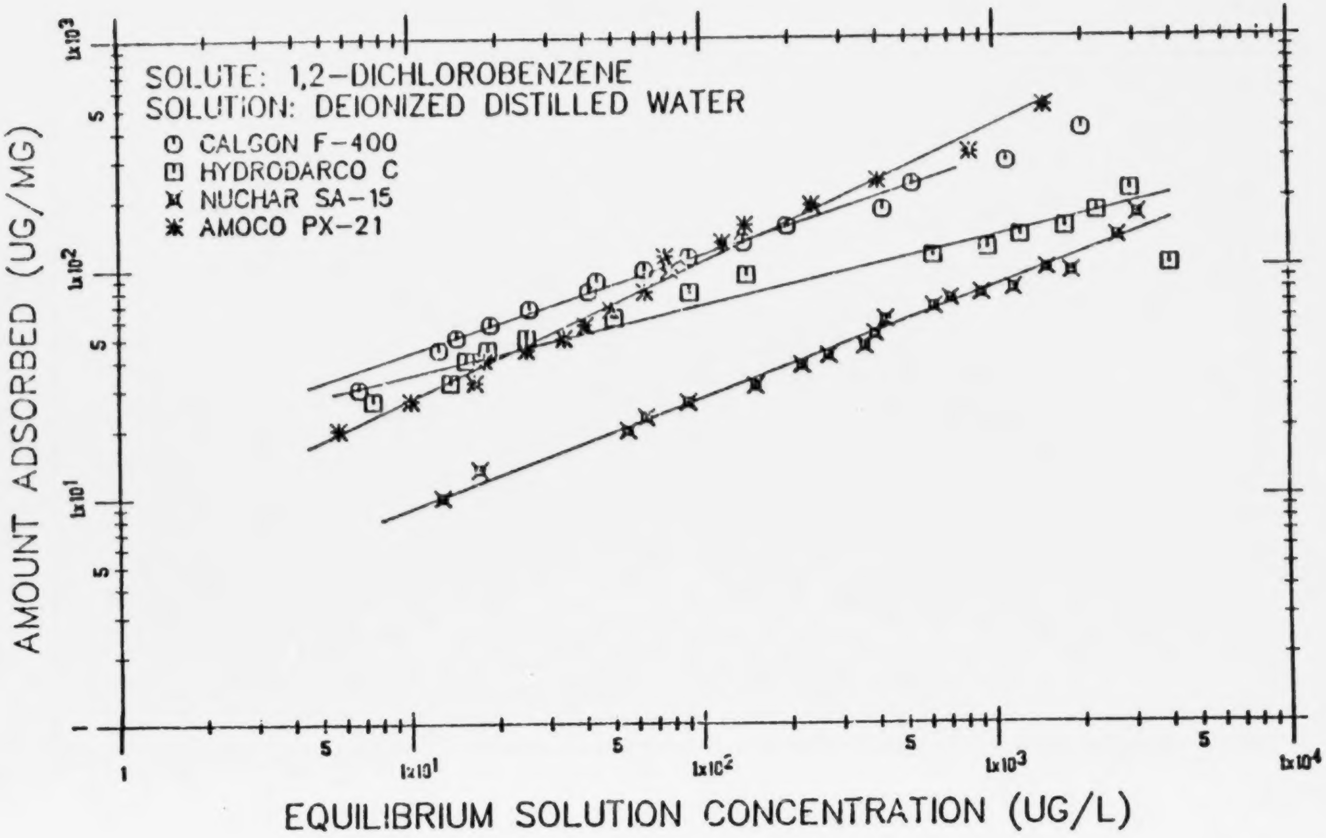


FIGURE 11-3. Experimental data and best-fit lines describing the adsorption of 1,2-dichlorobenzene from deionized-distilled water by various activated carbons.

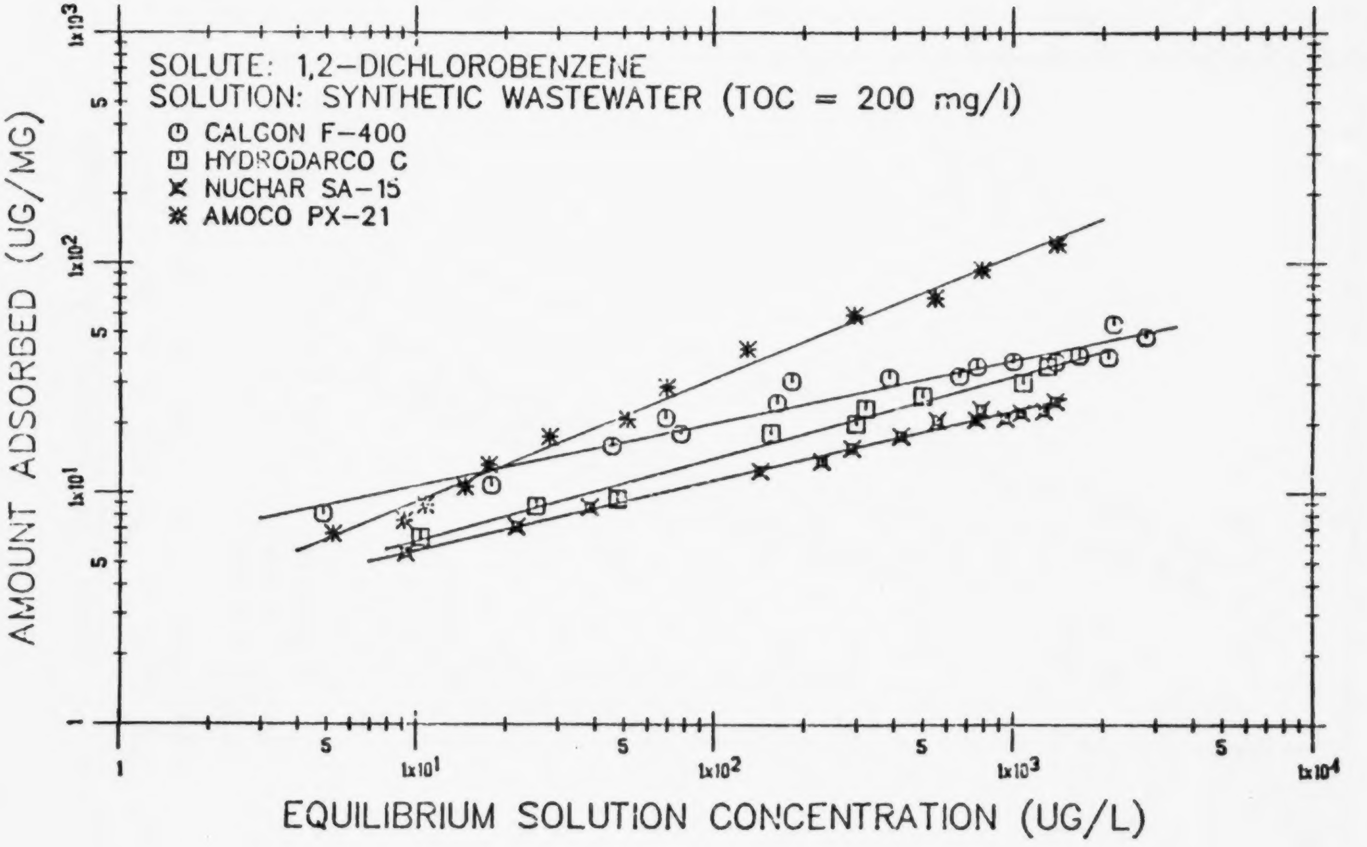


FIGURE 11-4. Experimental data and best-fit lines describing the adsorption of 1,2-dichlorobenzene from synthetic wastewater by various activated carbons.

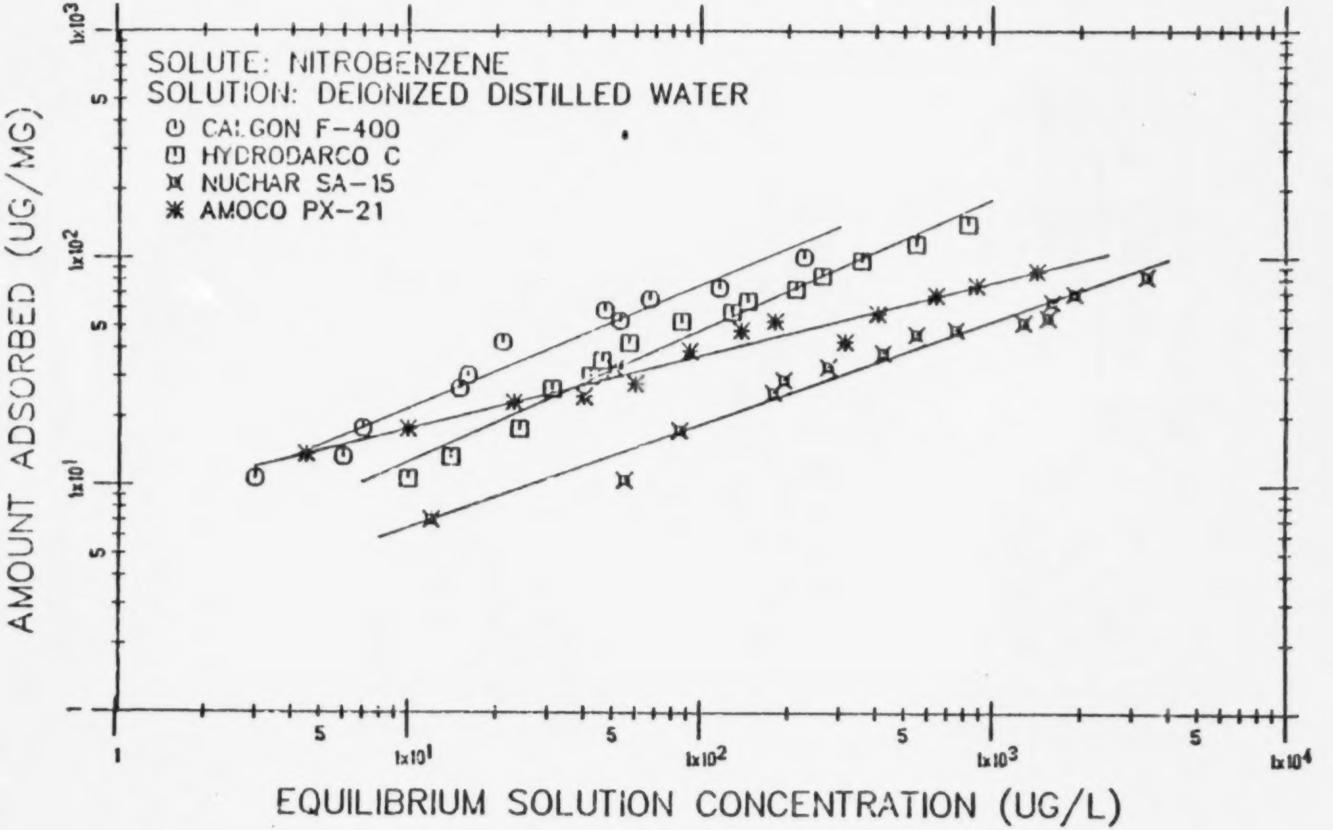


FIGURE II-5. Experimental data and best-fit lines describing the adsorption of nitrobenzene from deionized-distilled water by various activated carbons.

TABLE 11-1

PERTINENT OPERATING CONDITIONS USED DURING THE PAC/ACTIVATED SLUDGE BIOREACTOR STUDIES

Influent flow	29-31 ml/min.
Hydraulic retention time	5.4-5.6 hours
Aeration rate	3.8-4.4 l/min.
Influent TOC	95-110 mg/ℓ
Effluent TOC	10-20 mg/ℓ
MLSS (3-day SRT)	1800-2400 mg/ℓ
MLSS (6-day SRT)	3600-4200 mg/ℓ
MLSS (12-day SRT)	7500-8200 mg/ℓ
Influent toxics	100-200 μg/ℓ

TABLE 11-2

FREUNDLICH ISOTHERM PARAMETERS FOR ADSORPTION OF TOXIC ORGANICS BY HYDRODARCO C FROM CONTROL ACTIVATED SLUDGE BIOREACTOR EFFLUENT

Compound	K_f	1/n
Benzene	0.5	0.46
Toluene	1.2	0.47
Ethylbenzene	1.6	0.39
o-Xylene	1.1	0.47
Chlorobenzene	1.8	0.40
1,2-Dichlorobenzene	3.2	0.41
1,2,4-Trichlorobenzene	6.2	0.44
Lindane	4.0	0.39
Nitrobenzene	3.2	0.35

Results from equilibrium adsorption isotherm studies conducted with the remaining toxic organic compounds have been presented in Figures 11-6 through 11-8. Summaries of the Freundlich isotherm parameters for each compound in activated sludge effluent are given in Table 11-2.

Equilibrium isotherm studies were conducted to model the adsorption of wastewater TOC by Hydrodarco C. Results presented in Figures 11-9 to 11-11 and summarized by Table 11-3 showed that the organic constituents of the wastewater were not readily adsorbed by the powdered activated carbons.

Carbon adsorption rate studies were conducted to evaluate how rapidly the toxic organic compounds were adsorbed by powdered activated carbon. Results from representative rate studies with lindane and Hydrodarco C are given by Figures 11-12 through 11-14. As indicated by data in Figure 11-12, the adsorption of the lindane was characterized by a rapid reduction in aqueous concentration within the first 30 to 60 minutes. Greater than 90% of the total amount adsorbed at equilibrium was adsorbed within 1 to 2 hours. Equilibrium conditions were attained after 4 to 5 hours. Results shown by Figure 11-14 demonstrated that the rate of lindane adsorption in the experimental bioreactors was the same as occurred in a well-mixed batch reactor.

11.3 EFFECT OF PAC-ADDITION ON OVERALL TOC REMOVAL

Figure 11-15 compares data from the synthetic wastewater soluble TOC adsorption rate studies conducted with powdered carbon doses of 100, 1000, and 2000 mg/ℓ to soluble TOC degradation by activated sludge. Each of the studies was conducted in a 3.0-liter CMB reactor. The carbon adsorption studies were mixed at 300 rpm and compressed air was added to the TOC degradation study to maintain aerobic conditions. The data demonstrate that after 60 minutes the greatest amount of TOC removal occurred in the biodegradation study. A powdered activated carbon dose of 2000 mg/l was required to effect a TOC removal rate during the initial 30 minutes comparable to that which occurred due to biodegradation. The adsorption rate study with 100 mg/ℓ powdered carbon produced very little TOC removal compared to biodegradation. The largest powdered carbon dose used in the integrated studies was 200 mg/ℓ. On the basis of these studies, as well as the wastewater TOC adsorption isotherms, the powdered carbon doses used in the continuous flow bioreactor studies would appear to not significantly increase TOC removal over that observed in the control activated sludge units.

Previous investigations have shown that one of the benefits to accrue from the addition of the PAC to activated sludge is enhanced removal of overall organics as measured by BOD, COD, or TOC. Many of the studies reporting enhanced TOC removal by integrated activated sludge/carbon treatment systems were conducted with industrial wastewaters which are typically less biodegradable and more readily adsorbed by activated carbons than the synthetic wastewater used in this study to represent municipal wastewater.

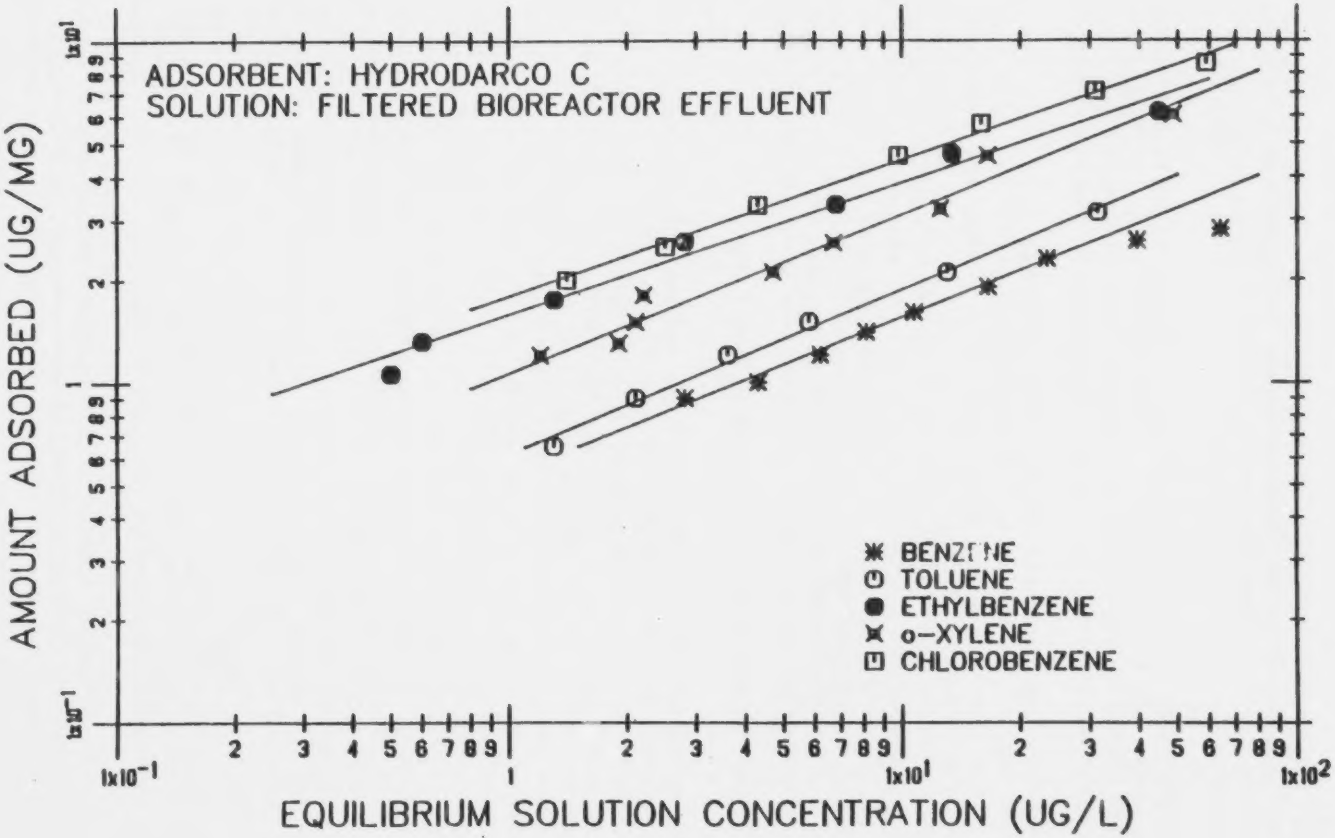


FIGURE 11-6. Experimental data and best-fit lines describing Freundlich isotherms for the adsorption of benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene from activated sludge bioreactor effluents by Hydrodarco C.

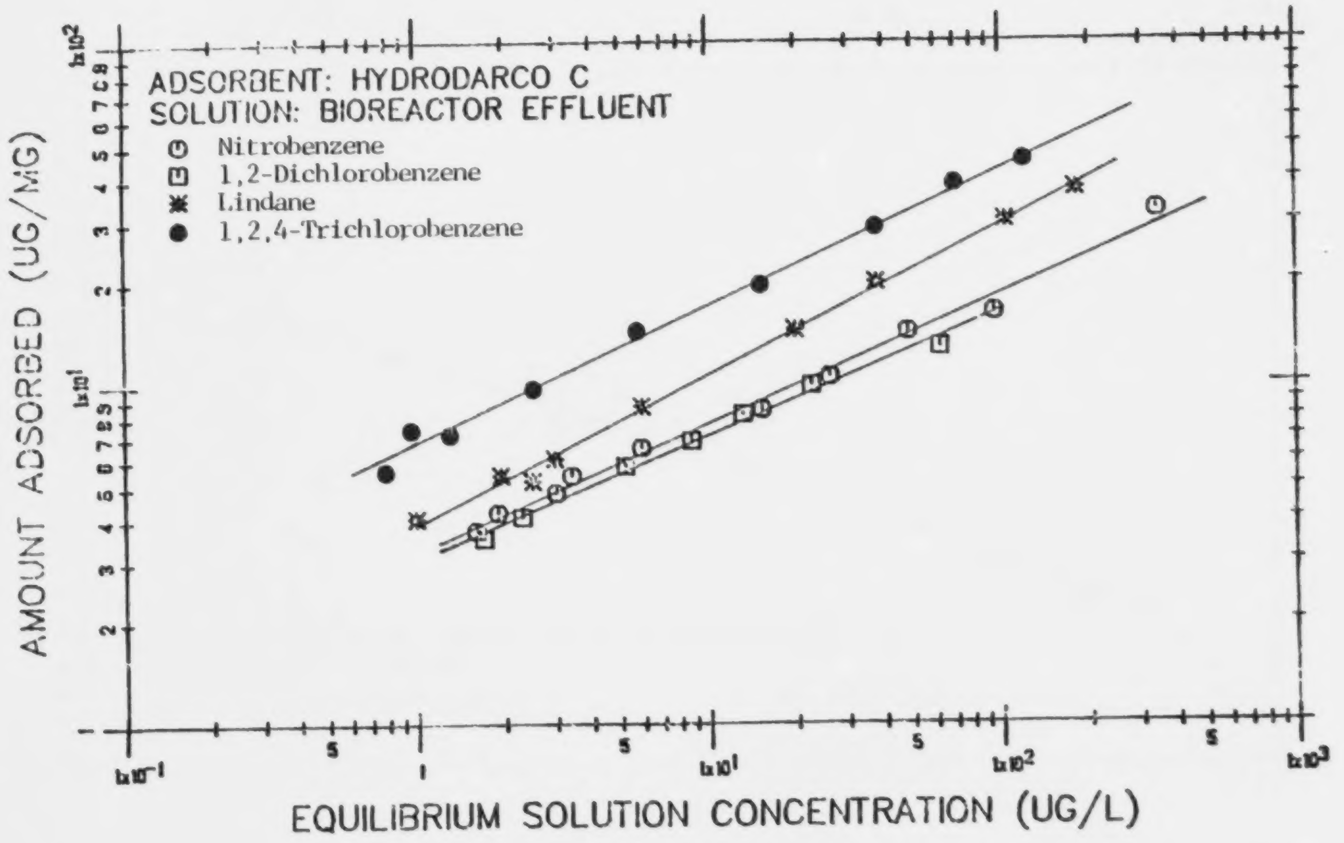


FIGURE 11-7. Experimental data and best-fit lines describing Freundlich adsorption isotherms for the adsorption of nitrobenzene, 1,2-dichlorobenzene, lindane, and 1,2,4-trichlorobenzene from activated sludge bioreactor effluents by Hydrodarco C.

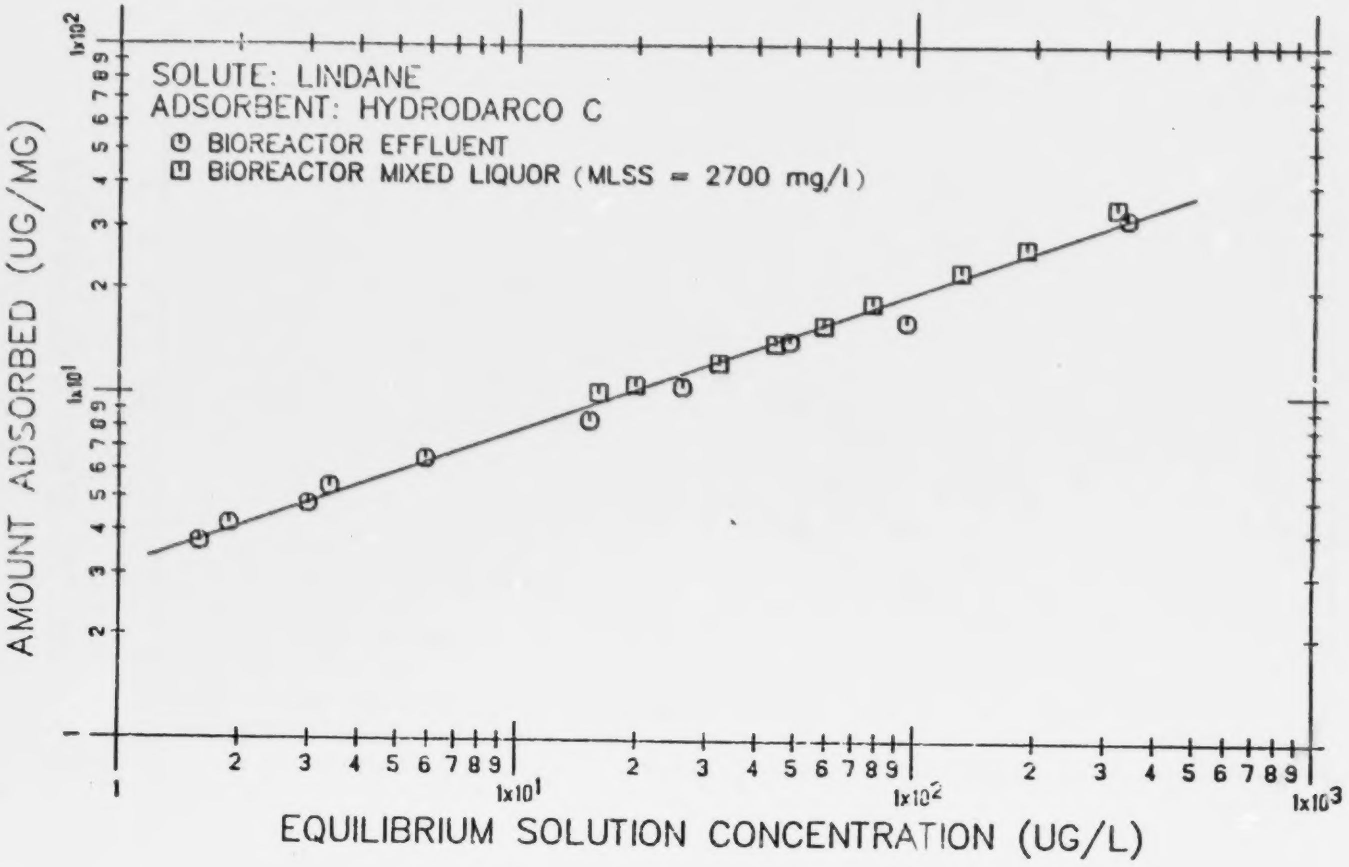


FIGURE 11-8. Experimental data and best-fit line describing the adsorption of lindane from activated sludge bioreactor effluent and activated sludge mixed liquor by Hydrodarco C

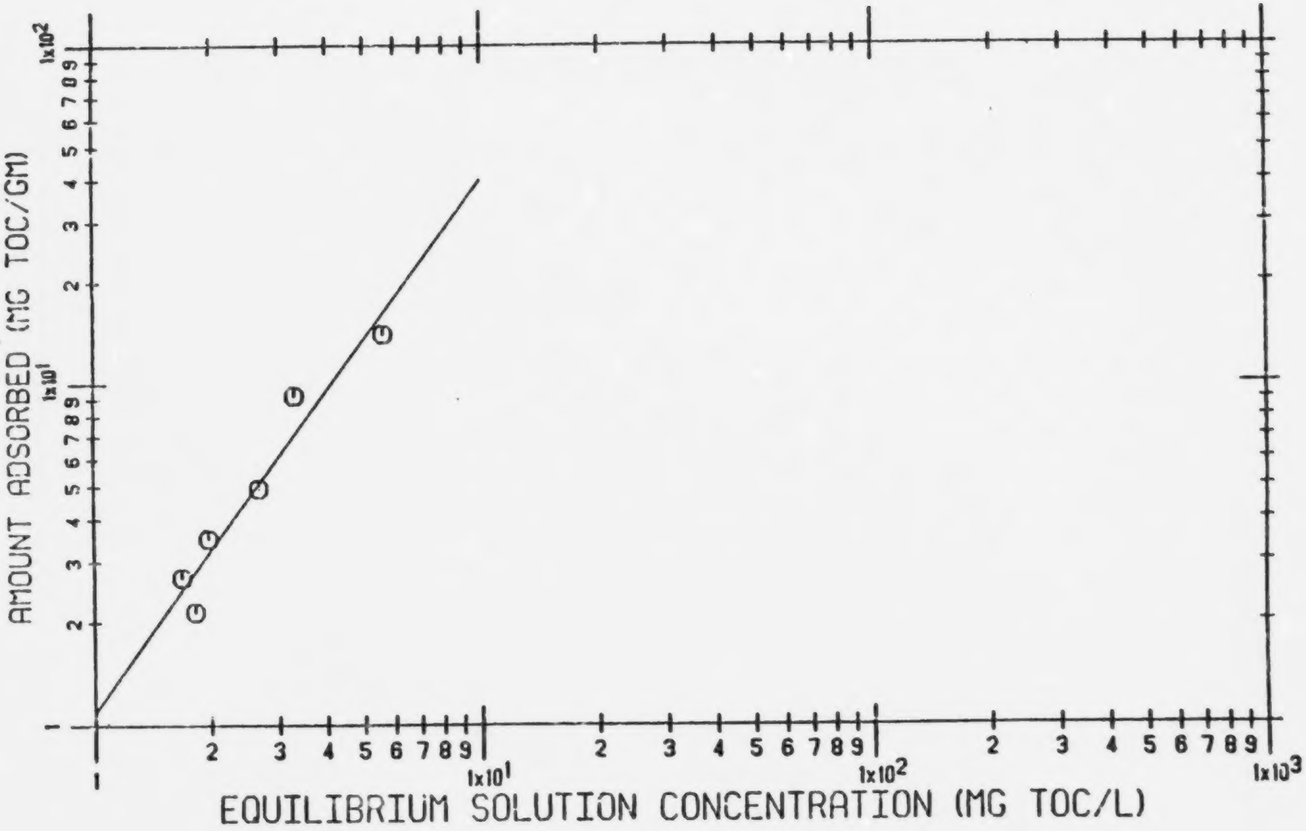


FIGURE 11-9 . Experimental data and best-fit line describing the adsorption of Ann Arbor wastewater treatment plant final effluent soluble TOC by Hydrodarco C.

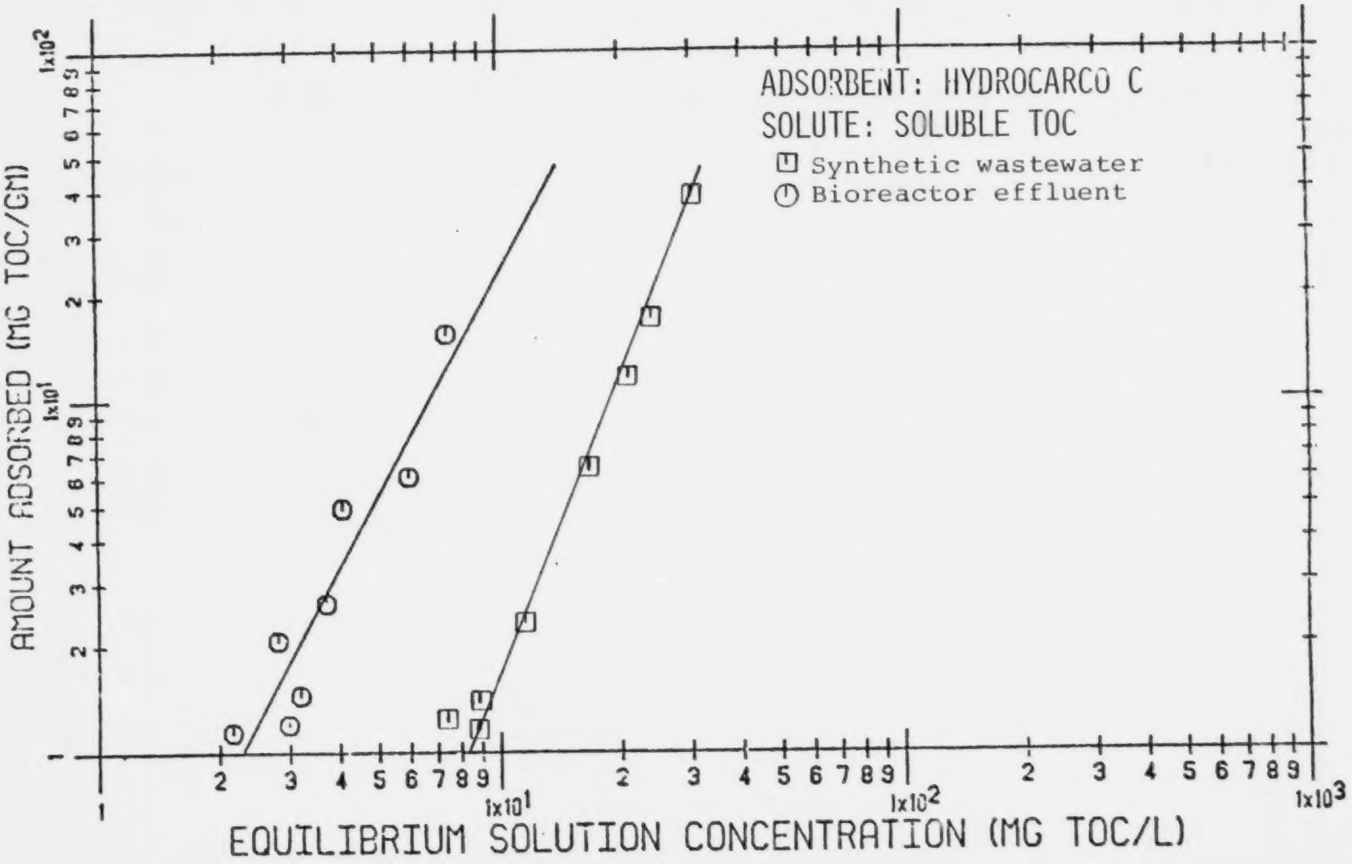


FIGURE 11-10. Experimental data and best-fit lines for adsorption of soluble TOC from synthetic wastewater and bioreactor effluent by Hydrodarco C.

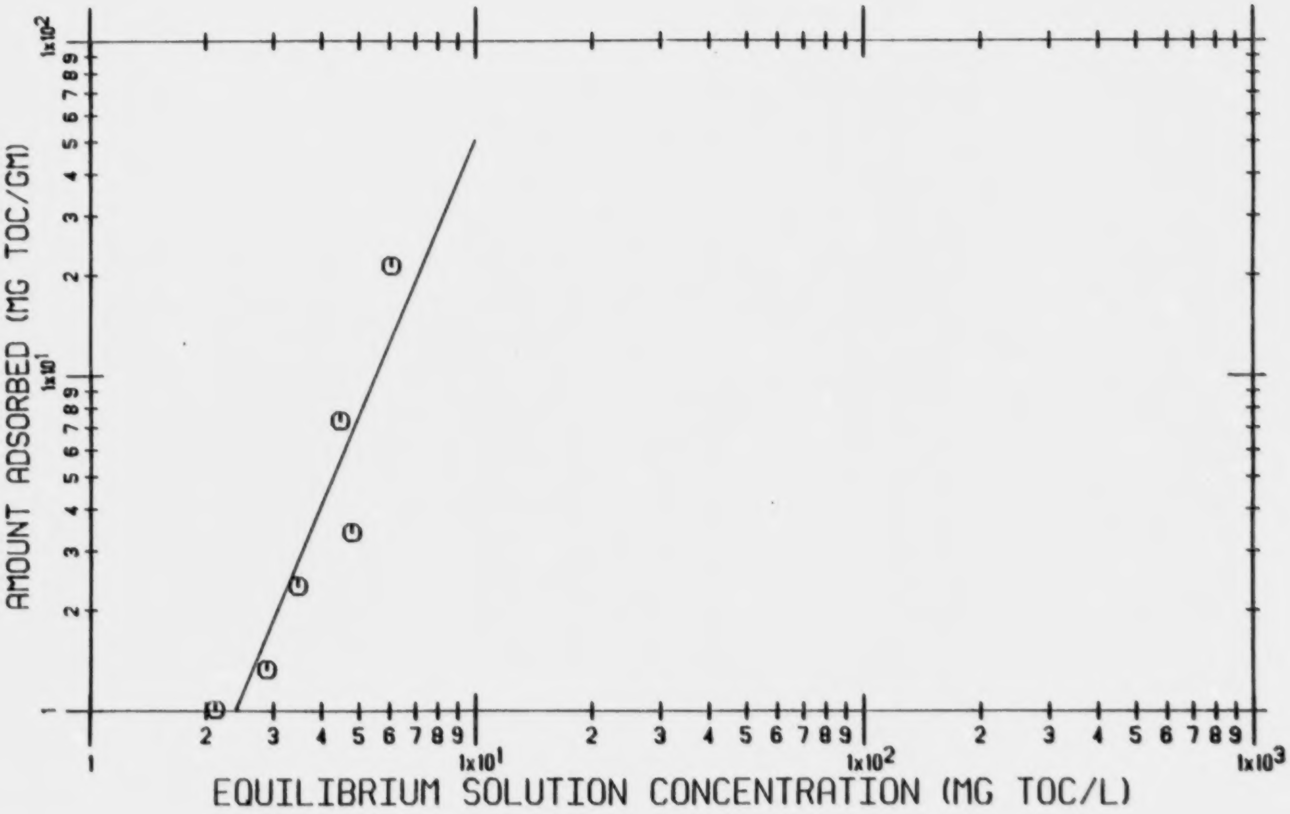


FIGURE 11-11. Experimental data and best-fit line describing the adsorption of effluent soluble TOC from a PAC-bioreactor receiving a 100 mg/l influent PAC dose by Hydrodarco C.

TABLE 11-3

FREUNDLICH PARAMETERS FOR WASTEWATER SOLUBLE TOC ADSORPTION BY HYDRODARCO C [+]

	K_f	$1/n$
synthetic wastewater	0.005	2.57
activated sludge effluent	0.175	2.12
Ann Arbor effluent	1.1	1.56
Effluent from 100 mg/l PAC bioreactor	0.092	2.74

[+] Freundlich constants calculated for C_e in mg/l and q_e in mg/g

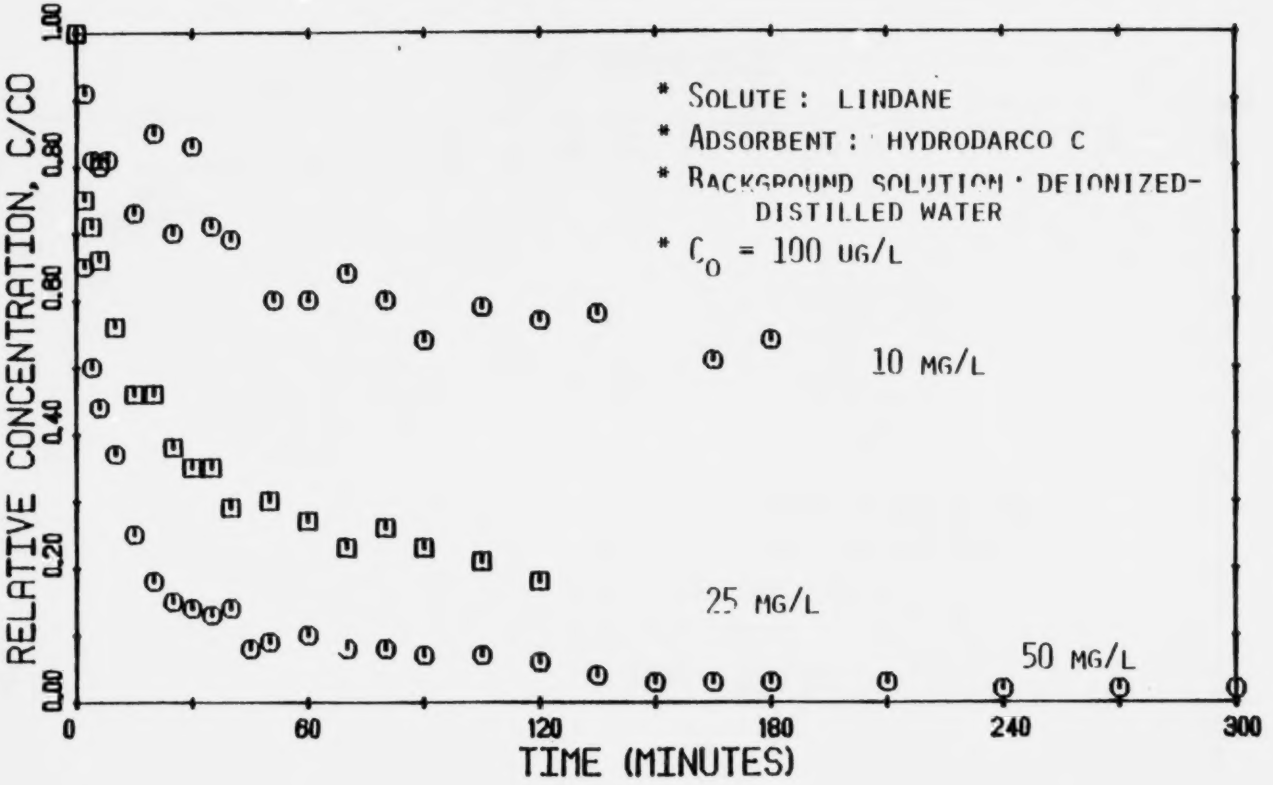


FIGURE 11-12 Typical results from lindane adsorption rate studies conducted in 3.0-liter completely-mixed batch (CMB) reactors.

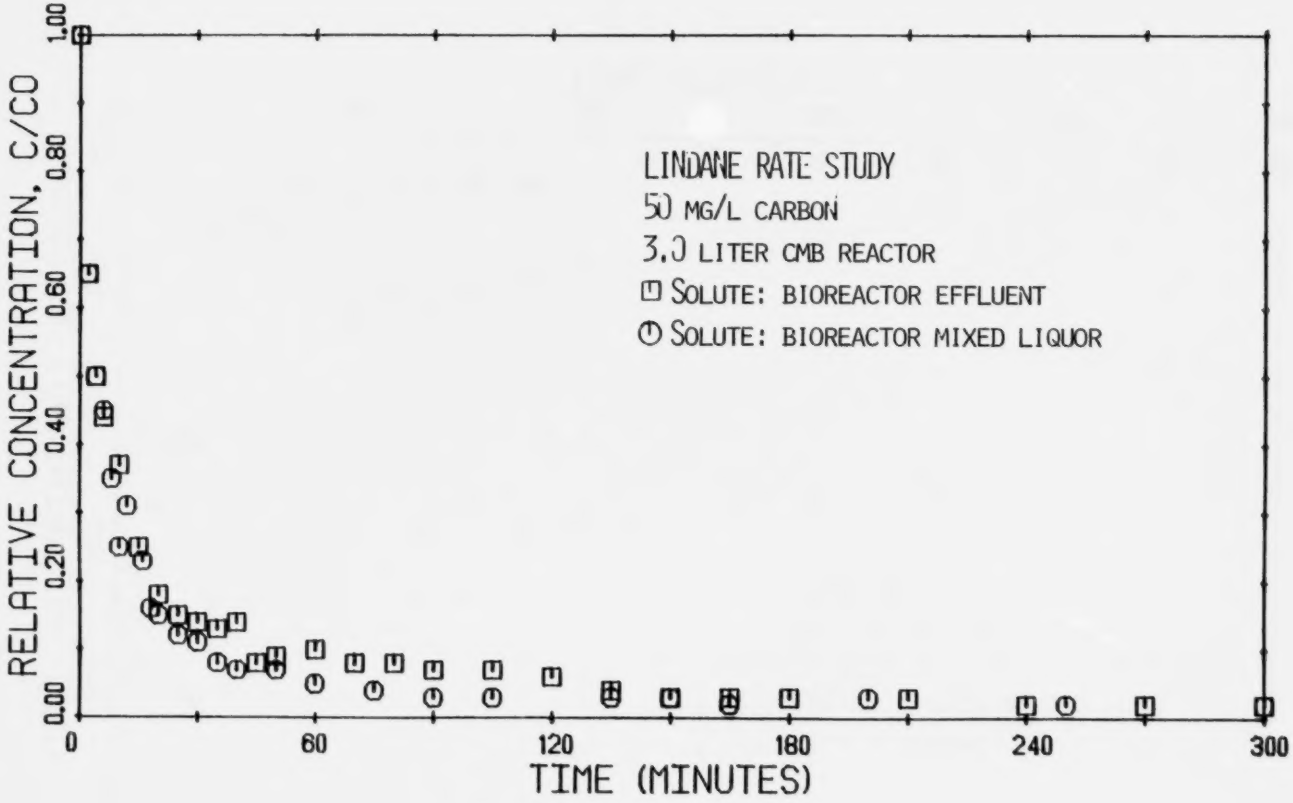


FIGURE 11-13. Comparison of results from lindane adsorption rate studies conducted in 3.0-liter completely-mixed batch reactors with background solutions of activated sludge bioreactor effluent and activated sludge mixed liquor. (Adsorbent: 50 mg/l of Hydrodarco C)

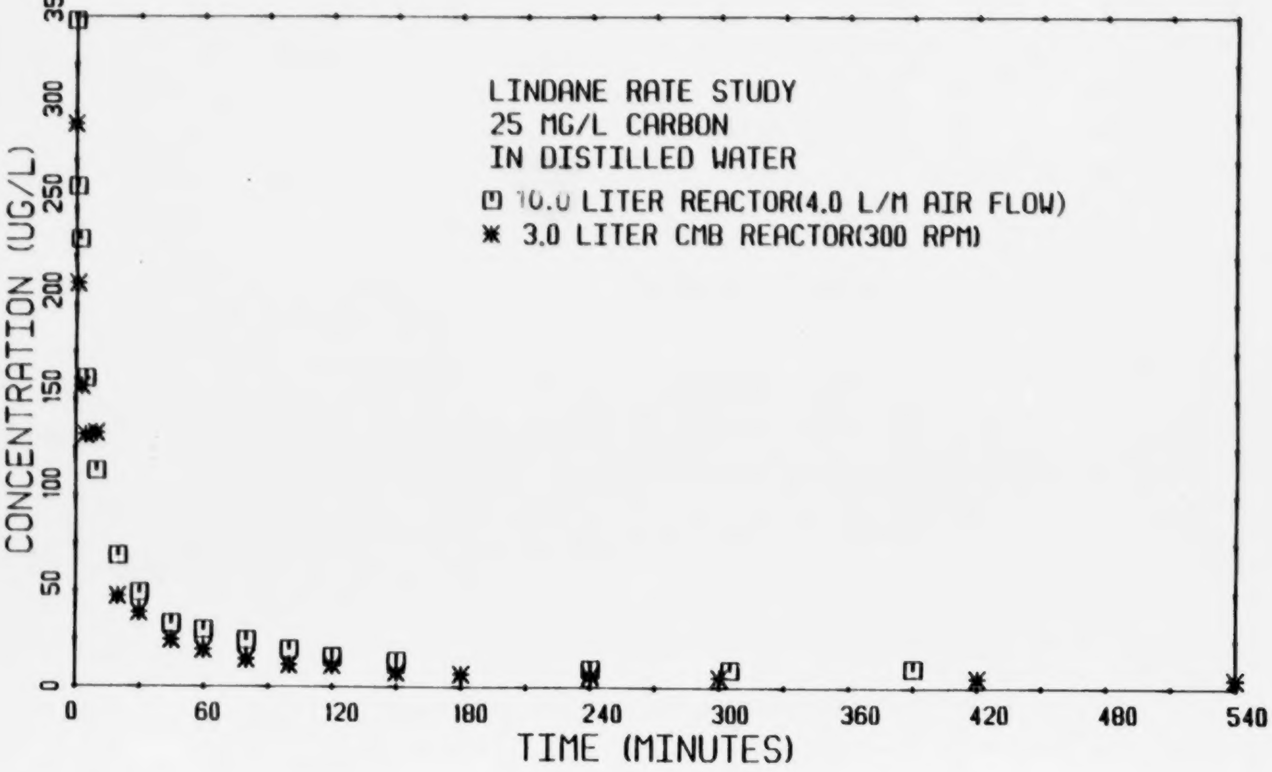


FIGURE 11-14. Comparison of results from lindane adsorption rate studies conducted in 3.0-liter completely-mixed batch reactor (mixed at 300 rpm) and a 10-liter bioreactor with a 4.0 liter/min aeration rate (batch mode).

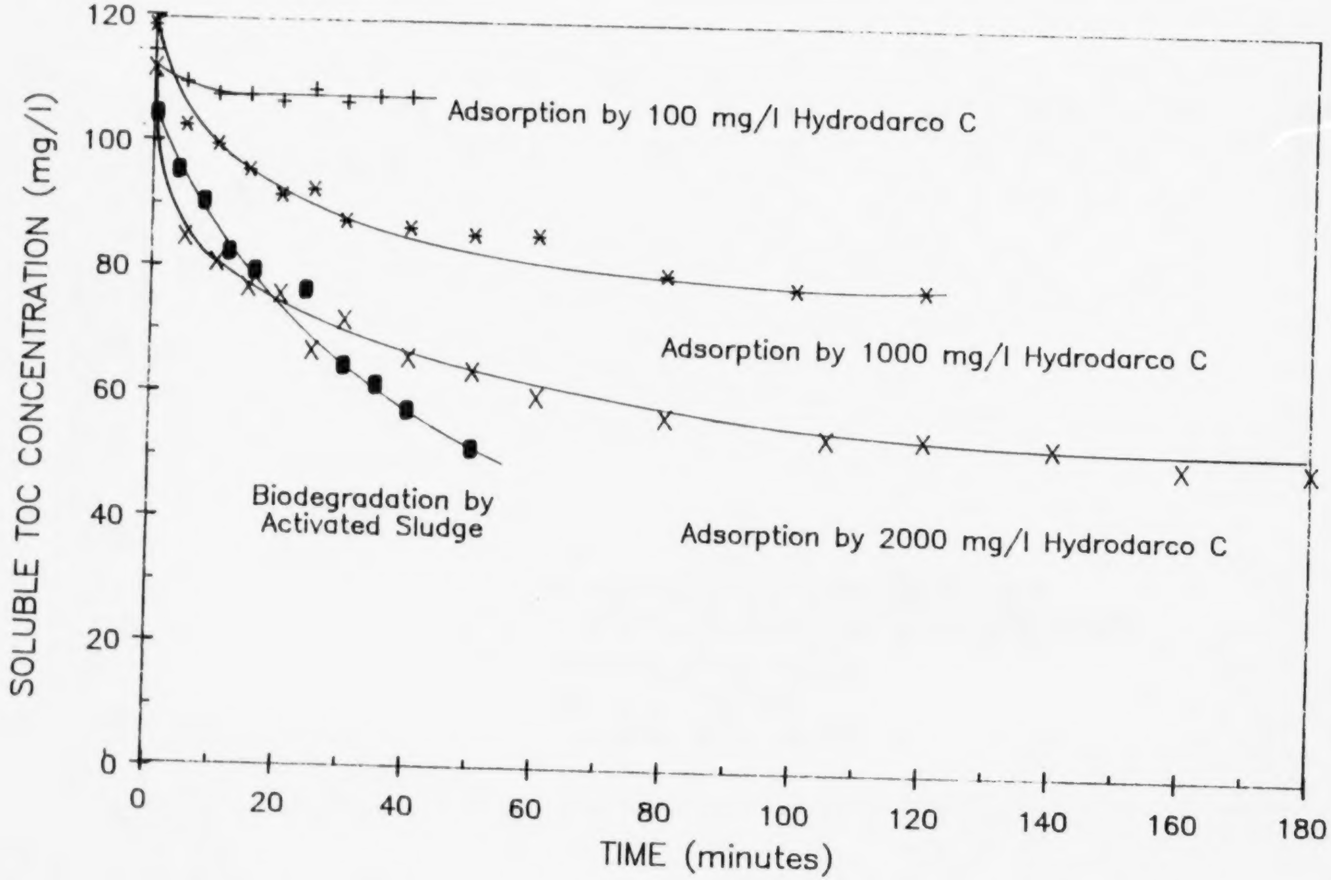


FIGURE 11 - 15. Comparison of synthetic wastewater soluble TOC biodegradation by activated sludge to removal by adsorption by Hydrodarco C.

Influent and effluent TOC samples were typically taken every three to five days during steady-state bioreactor operating conditions. Typical TOC removals ranged between 80 and 90% for all of the PAC bioreactor studies conducted with influent PAC concentrations from 25 to 100 mg/ℓ. Results from PAC studies with influent PAC doses up to 100 mg/ℓ showed no significant increase in TOC removal compared to control studies without PAC.

11.4 REMOVAL OF NON-BIODEGRADABLE TOXIC ORGANIC COMPOUNDS

Integrated activated sludge/carbon adsorption bioreactor studies to be described in this section include the non-biodegradable compounds lindane and 1,2,4-trichlorobenzene and the poorly biodegraded compound 1,2-dichlorobenzene. Results from the activated sludge studies presented in Section 8 indicated that lindane and 1,2,4-trichlorobenzene were not biodegradable in the experimental activated sludge system. While nearly complete recoveries of both compounds from the activated sludge units were possible, their fate was quite different. Very little reduction in the aqueous concentration of lindane occurred during activated sludge treatment. Typically, effluent concentrations averaged 93 to 95% of the influent value. Results for 1,2,4-trichlorobenzene were quite different, however; effluent concentrations averaged only 10 to 12% of the influent value. The approximate 90% reduction in the aqueous 1,2,4-trichlorobenzene concentration that occurred during activated sludge treatment was due to volatilization from the activated sludge bioreactors. Baseline studies demonstrated that near complete recovery of the amount of 1,2,4-trichlorobenzene volatilized was possible. Although 1,2-dichlorobenzene was found to be partially removed by biodegradation in activated sludge studies, its behavior in the PAC bioreactor studies was more similar to 1,2,4-trichlorobenzene than the readily biodegradable compounds.

11.4.1 Non-volatile Compound

Lindane was used as a model non-volatile, non-biodegradable compound for the PAC bioreactor studies. Results from activated sludge studies showed only small (~5%) reductions in aqueous concentration occurred due to sorption of lindane by the activated sludge biomass. Integrated activated sludge/carbon absorption studies were conducted under two different bioreactor operating conditions. Initial bioreactor studies utilized the 10-liter experimental bioreactors which received the synthetic wastewater solution. A second set of continuous flow studies were conducted in 3-liter bioreactors, described in Section 5, which received primary effluent from the Ann Arbor wastewater treatment facility.

11.4.1.1 Synthetic Wastewater Studies; 10-liter Bioreactors

The effect of influent PAC concentration on the removal of lindane in the 10-liter bioreactors receiving synthetic wastewater was evaluated at influent Hydroarco C concentrations of 12.5, 25, and 50 mg/ℓ and influent SA-15 concentrations of 25 and 50 mg/ℓ. The bioreactors were operated with 3 day solids retention times and 5.5 hour hydraulic retention times.

Results from the PAC studies with Hydrodarco C have been compared with results from control activated sludge studies in Figures 11-16, 11-17 and 11-18 for influent PAC doses of 12.5, 25, and 50 mg/ℓ, respectively. Each figure presents influent and effluent concentrations and C_e/C_i values representing the ratio of effluent concentration to influent concentration. Day Zero in each figure represents the initiation of both the lindane and PAC slurry flows to the influent. Each study was conducted for a total of four to eight weeks.

The results given in Figures 11-16 through 11-18 indicate that the removal of lindane due to adsorption by the activated carbon increased with increasing influent PAC concentration. A significant finding was that a PAC dose as small as 12.5 mg/ℓ effected an approximate 68% reduction in effluent lindane concentration. Mean influent and effluent concentrations for the 12.5 mg/ℓ PAC study were 104 and 34 μg/ℓ, respectively. Increasing the influent PAC dose to 25 mg/ℓ resulted in an 84% reduction of lindane as influent and effluent concentrations averaged 98.2 and 15.2 μg/ℓ respectively. Greater than a 90% lindane removal was recorded when an influent PAC concentration of 50 mg/ℓ was used. The effluent concentration in 50 mg/ℓ PAC study averaged 8.2 μg/ℓ while the influent concentration averaged 101 μg/ℓ. Figure 11-19 provides a comparison of overall lindane removals for the three PAC bioreactor studies with Hydrodarco C. Summaries of mean influent and effluent concentrations are given in Table 11-4.

Results from the PAC bioreactor studies with SA-15 have been compared to results from control activated sludge studies in Figures 11-20 and 11-21 for influent PAC doses of 25 and 50 mg/ℓ, respectively. Lindane removals averaged 83.4 and 91.1% during the 25 and 50 mg/ℓ PAC studies, respectively, compared with 3.5% during the control activated sludge study. Figure 11-22 provides a comparison of overall removals observed during the two SA-15 bioreactor studies. Summaries of mean influent and effluent concentrations for the control, 25 and 50 mg/ℓ SA-15 bioreactor studies were included in Table 11-4.

Equilibrium adsorption isotherm studies conducted with lindane in bioreactor effluent indicated that for a given aqueous concentration more lindane was adsorbed by SA-15 than Hydrodarco C. Results from the CMF PAC bioreactor studies demonstrated, however, that there were no significant differences in lindane removal between bioreators receiving SA-15 and Hydrodarco C. Figures 11-23 and 11-24 provide comparisons of effluent lindane concentrations and C/C_0 values from bioreactor studies with 25 and 50 mg/ℓ, respectively, of SA-15 and Hydrodarco C. For a given PAC dose, SA-15 and Hydrodarco C effected the same level of lindane removal. The plot of percent removal versus PAC dose in Figure 11-25 shows the similarity in performances of the two commercial powdered activated carbons Hydrodarco C and SA-15, and the superior performance of the experimental high surface

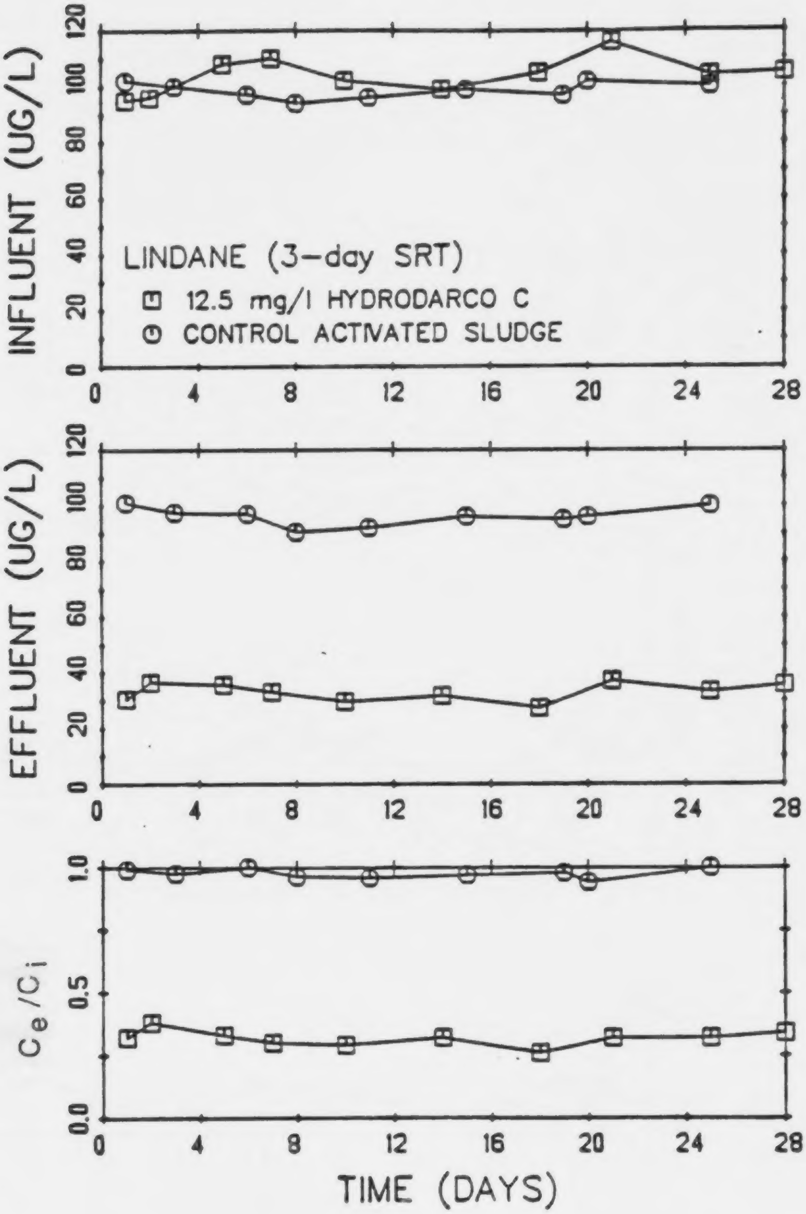


FIGURE 11-16. Effect of a 12.5 mg/l influent Hydrodarco C dose on the effluent lindane concentration from a 10-liter bioreactor.

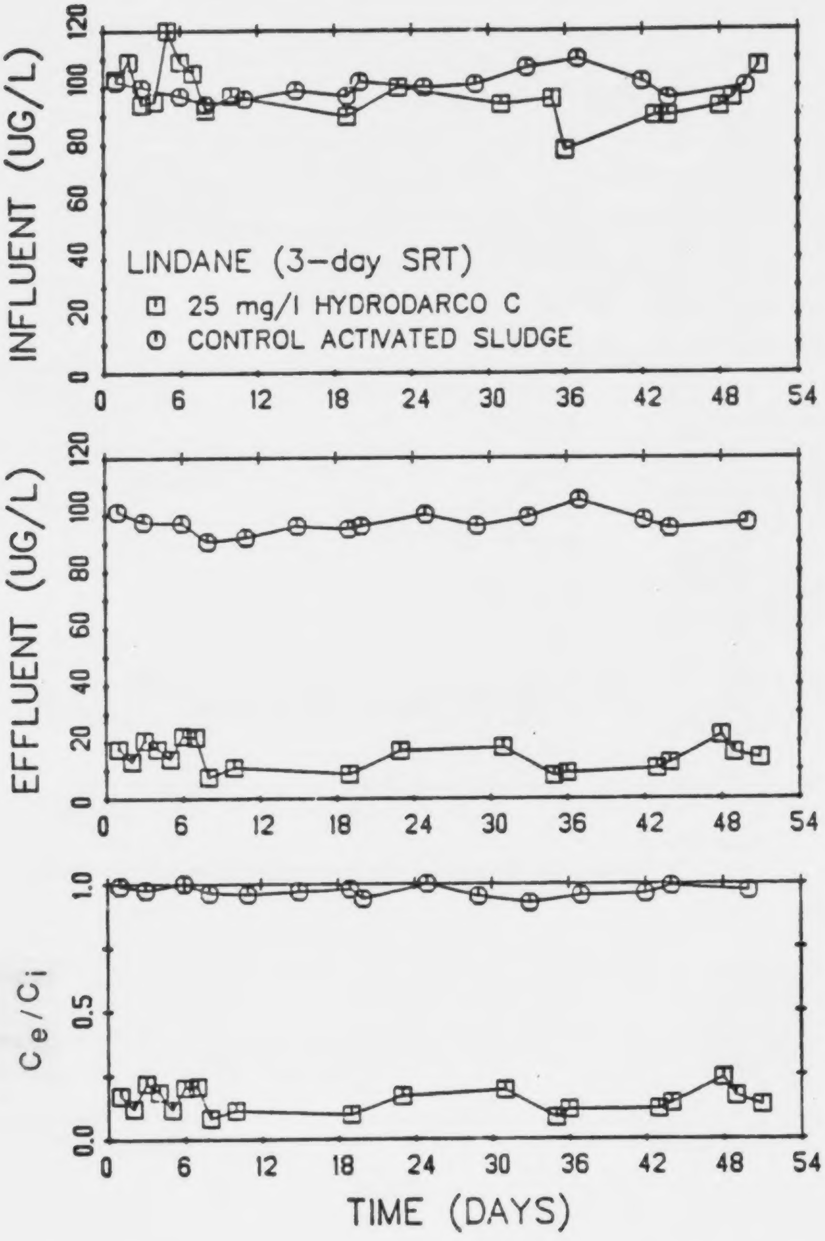


FIGURE 11-17. Effect of a 25 mg/l influent Hydrodarco C dose on the effluent lindane concentration from a 10-liter bioreactor.

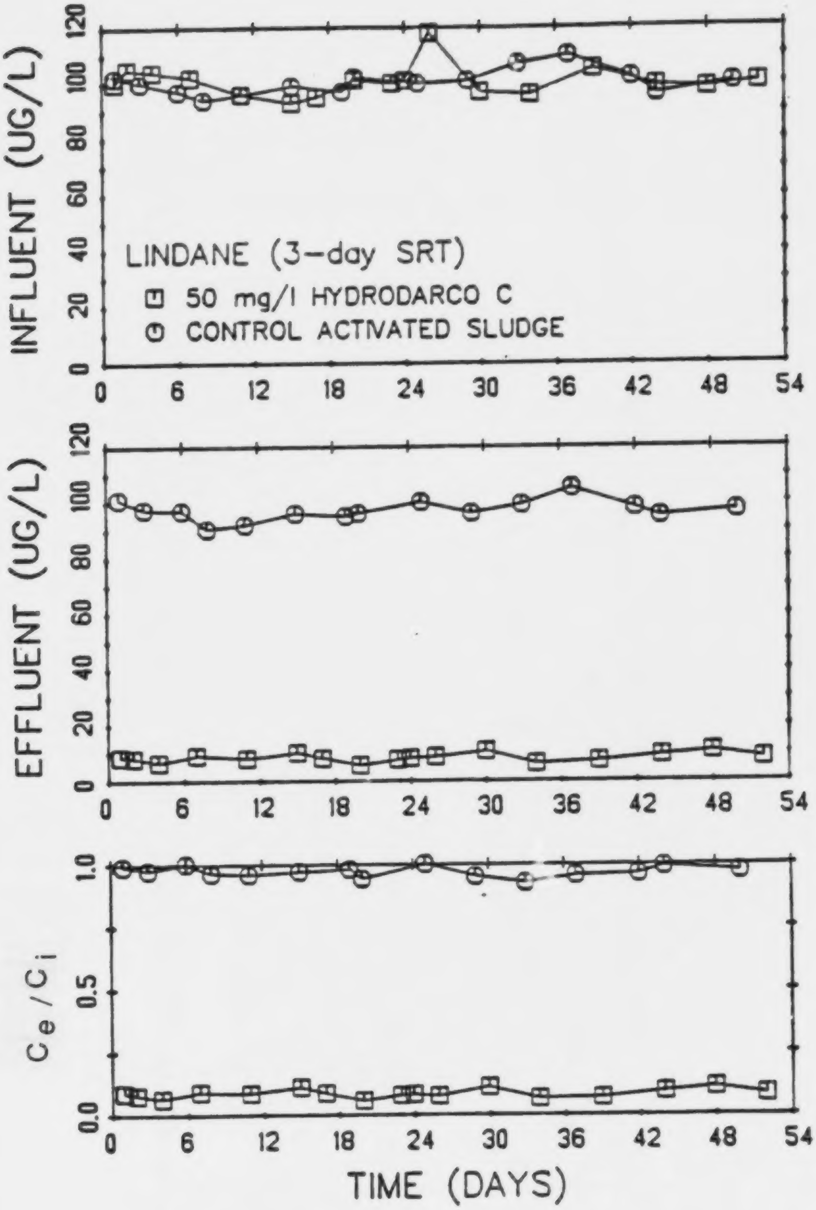


FIGURE 11-18. Effect of a 50 mg/l influent Hydrodarco C dose on the effluent lindane concentration from a 10-liter bioreactor.

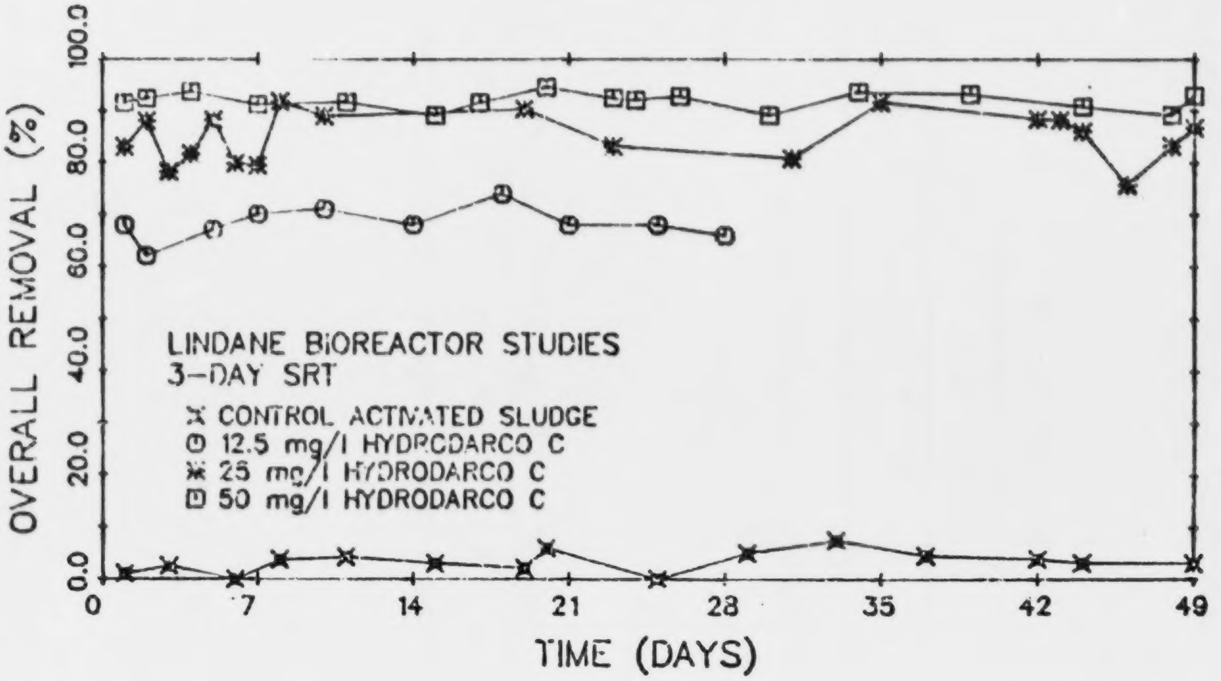


FIGURE 11-19. Comparison of lindane removals measured during a control activated sludge study and PAC-bioreactor studies with influent Hydrodarco C doses of 12.5, 25, and 50 mg/l.

TABLE 11-4

EFFECT OF INFLUENT PAC DOSE ON EFFLUENT LINDANE CONCENTRATIONS FROM 10-LITER BIOREACTORS WITH 3-DAY SRT'S

Influent Carbon Dose (mg/ℓ)	Influent Conc. (μg/ℓ)		Effluent Conc. (μg/ℓ)		Removal (%)
	Mean	S.D.	Mean	S.D.	Mean
	HYDRODARCO C				
0	100	4.2	96.9	3.6	3.3
12.5	104	6.4	33.7	2.7	67.6
25	98.2	8.8	15.2	4.8	84.5
50	101	5.7	8.2	1.4	91.8
	SA-15				
0	93.9	4.1	90.6	3.6	3.5
25	89.0	7.0	15.0	2.3	83.2
50	97.2	4.1	8.1	2.0	91.7
	PX-21				
15	94.8	6.3	13.2	3.4	86.1
30	96.1	7.1	4.7	2.1	95.1

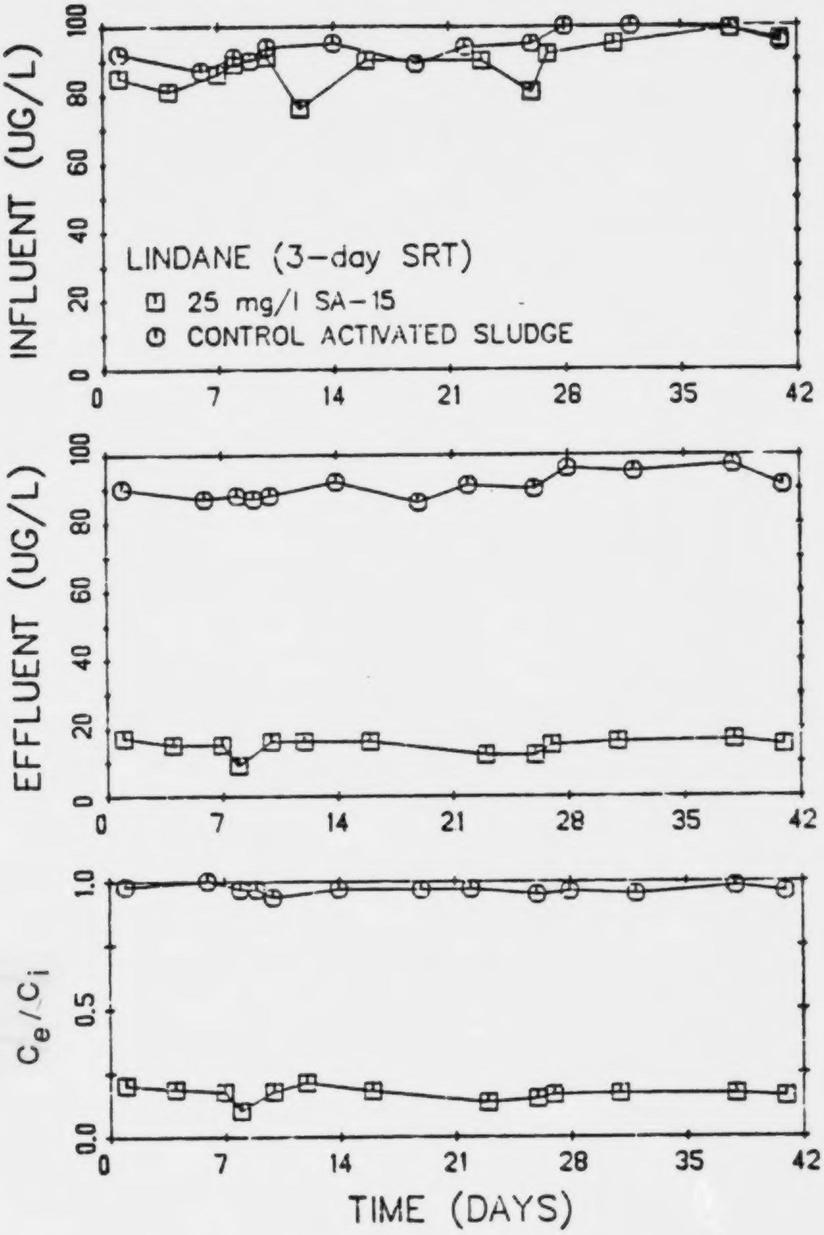


FIGURE 11-20. Effect of a 25 mg/l influent SA-15 dose on the effluent lindane concentration from a 10-liter bioreactor.

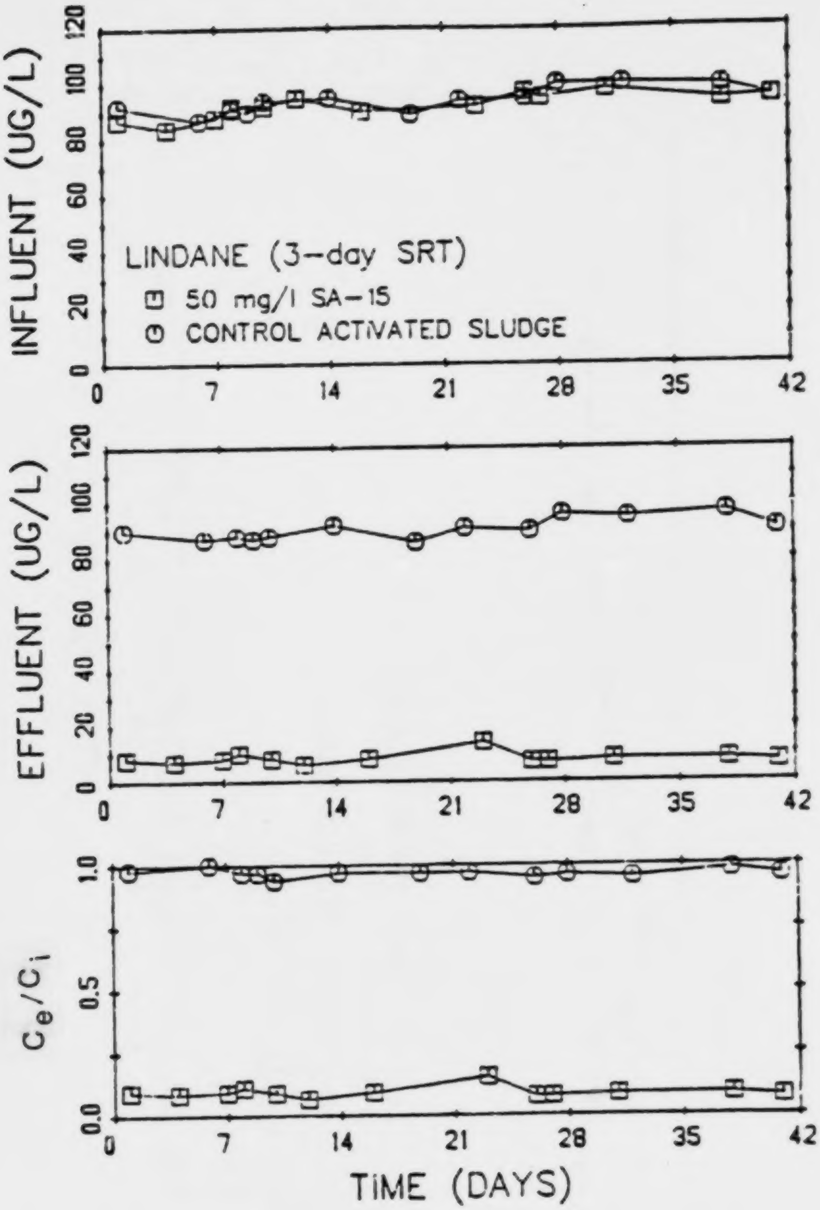


FIGURE 11-21. Effect of a 50 mg/l influent SA-15 dose on the effluent lindane concentration from a 10-liter bioreactor.

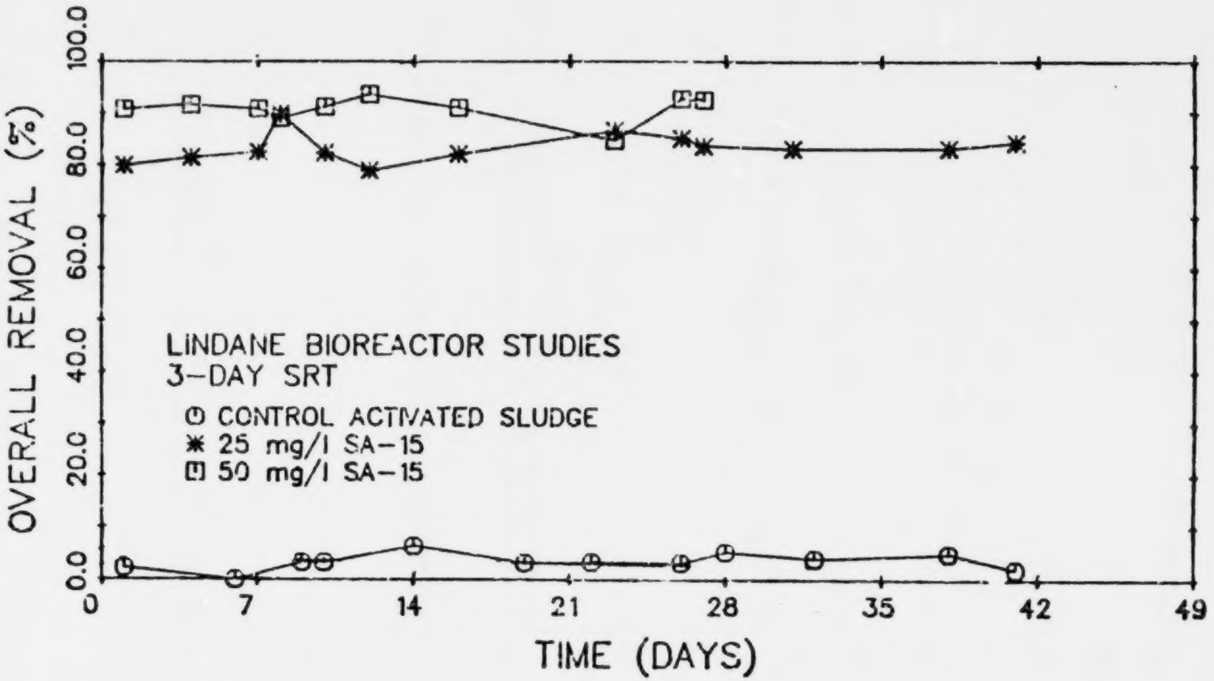


FIGURE 11-22. Comparison of lindane removals measured during a control activated sludge bioreactor study and PAC-bioreactor studies with influent SA-15 doses of 25 and 50 mg/l.

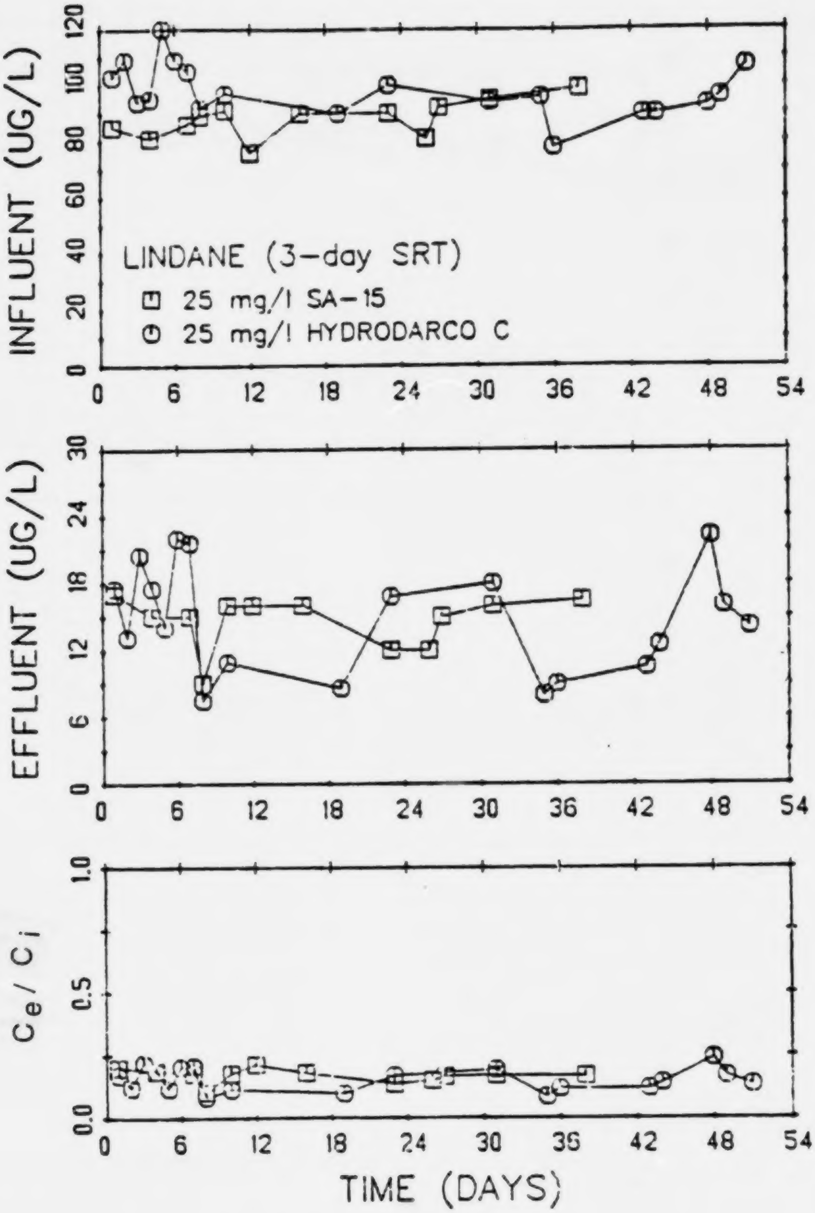


FIGURE 11-23. Comparison of lindane effluent concentrations from PAC-bioreactor studies with 25 mg/l influent PAC doses of Hydrodarco C and SA-15.

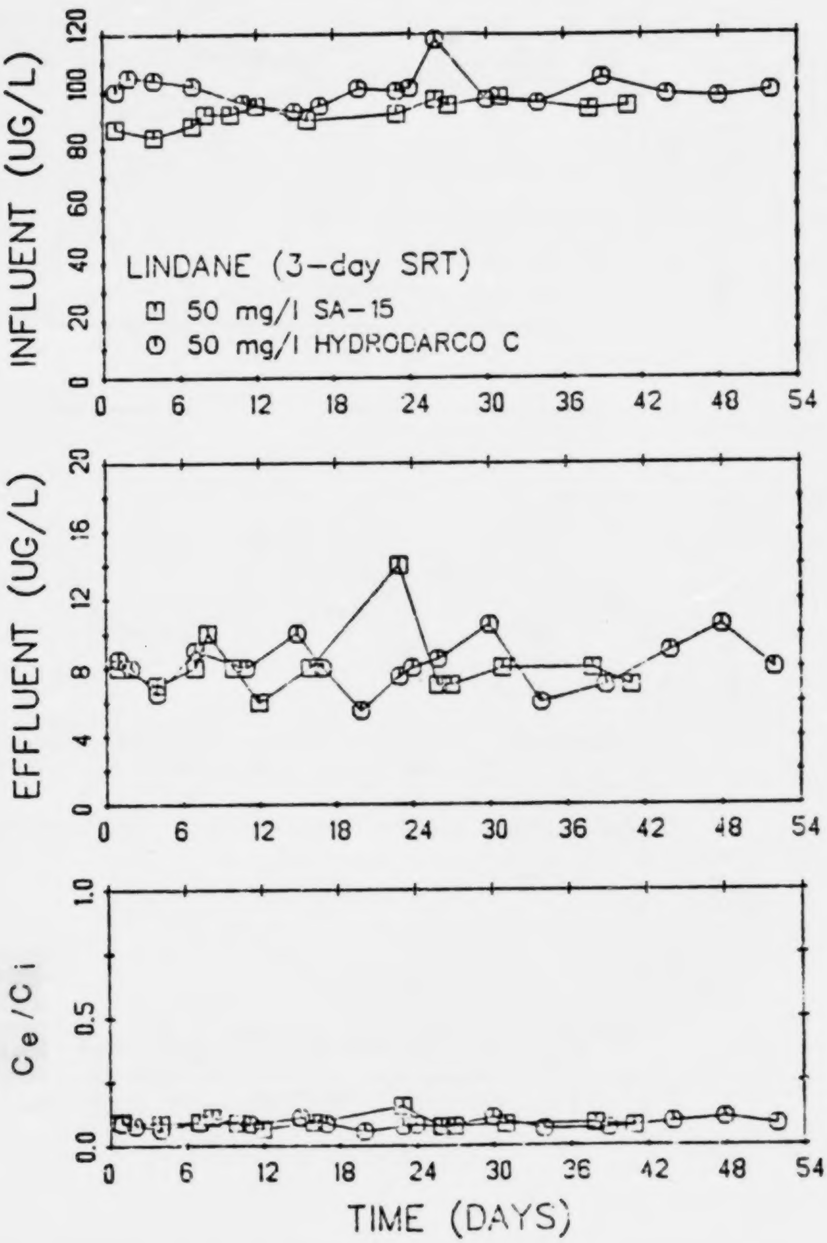


FIGURE 11-24. Comparison of lindane effluent concentrations from PAC-bioreactor studies with 50 mg/l influent PAC doses of Hydrodarco C and SA-15.

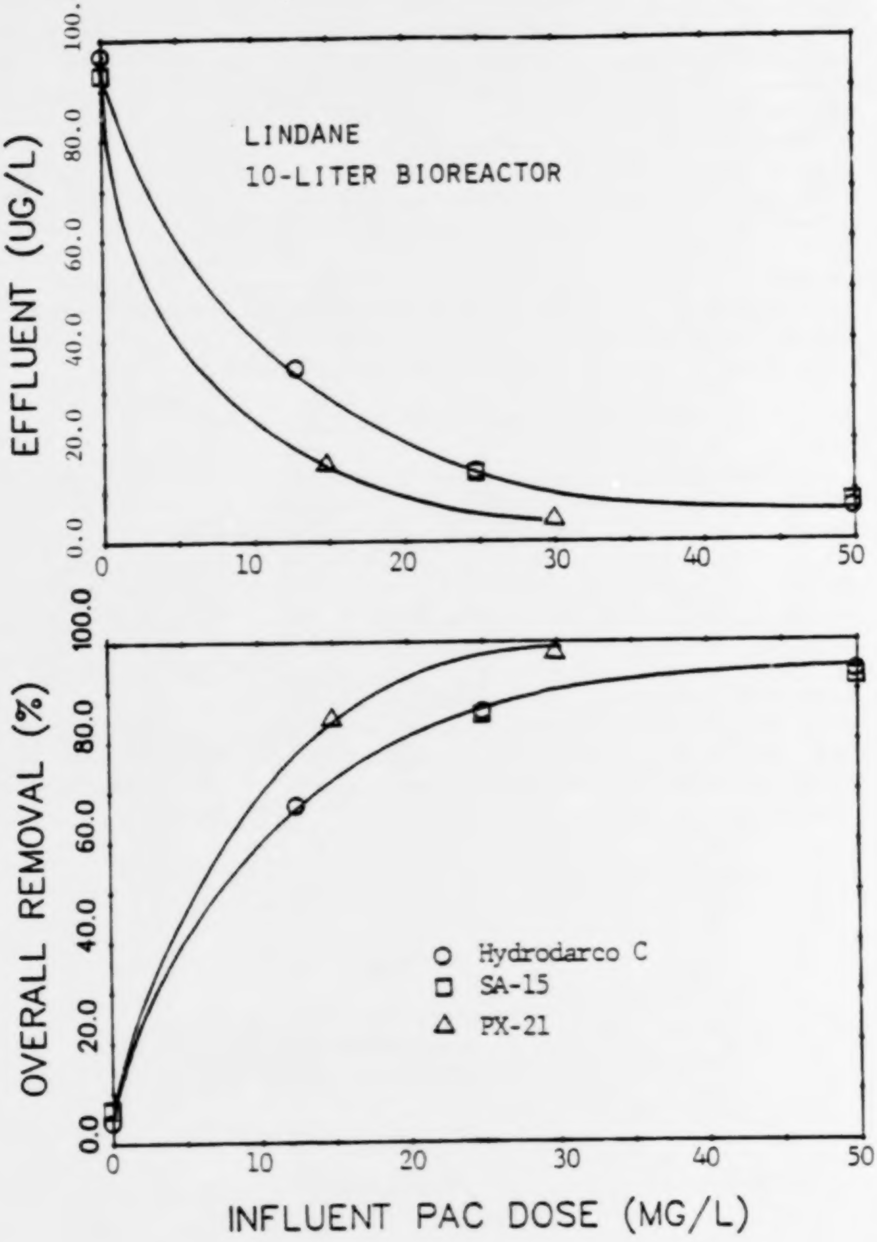


FIGURE 11-25. Effect of influent PAC doses of Hydrodarco C, SA-15, and PX-21 on lindane effluent concentration and overall removals

area PAC, PX-21. Figure 11-25 also shows that the incremental improvement in lindane removal decreased with increasing PAC dose. While the total amount of lindane removed from solution increased with increasing PAC dose, the amount adsorbed per unit weight of activated carbon decreased. As shown by Table 11-5, the amount of lindane removed increased from approximately 70 μg/ℓ to over 90 μg/ℓ with an increase in PAC dose from 12.5 mg/ℓ to 50 mg/ℓ. The amount of lindane adsorbed per unit weight of activated carbon decreased from 5.6 μg adsorbed/mg PAC to less than 2.0 μg/mg. Thus, the larger the PAC dose for a given influent lindane concentration, the less effectively the adsorptive capacity for lindane can be utilized. Such a result is expected in a CMF reactor. A larger PAC dose produces a smaller steady state aqueous mixed liquor or effluent concentration. As the aqueous concentration decreases, the driving force for adsorption by the activated carbon decreases, resulting in a smaller amount adsorbed per unit weight of carbon.

11.4.1.2. Ann Arbor Primary Effluent Wastewater

Powdered activated carbon bioreactor studies with Ann Arbor primary effluent were conducted in 3-liter reactors with Hydrodarco C, SA-15, and PX-21. The reactor conditions were as outlined in Table 11-1 with a 6-day SRT. Influent PAC concentrations of 15 and 30 mg/ℓ of Hydrodarco C, 30 mg/ℓ of SA-15, and 15 and 30 mg/ℓ of PX-21 were examined in the 3-liter units. A summary of results from the 3-liter PAC bioreactor studies with Ann Arbor wastewater is given by Table 11-6. At a given PAC dose effluents from bioreactors receiving Hydrodarco C and SA-15 were the same, while the effluent from the bioreactor receiving the experimental, high surface area PAC, PX-21, was consistently lower. An influent PAC dose of 15 mg/ℓ PX-21 effected an average lindane removal of 98% compared with 73% for Hydrodarco C.

TABLE 11-5

EFFECT OF PAC DOSE ON LINDANE
ADSORPTION PER WEIGHT
OF ACTIVATED CARBON (μg/mg)

PAC Dose (mg/ℓ)	Hydrodarco C		SA-15	
	μg/ℓ	μg/mg	μg/ℓ	μg/mg
12.5	70	5.6	--	--
25	83	3.3	74	3.0
50	93	1.9	89	1.8

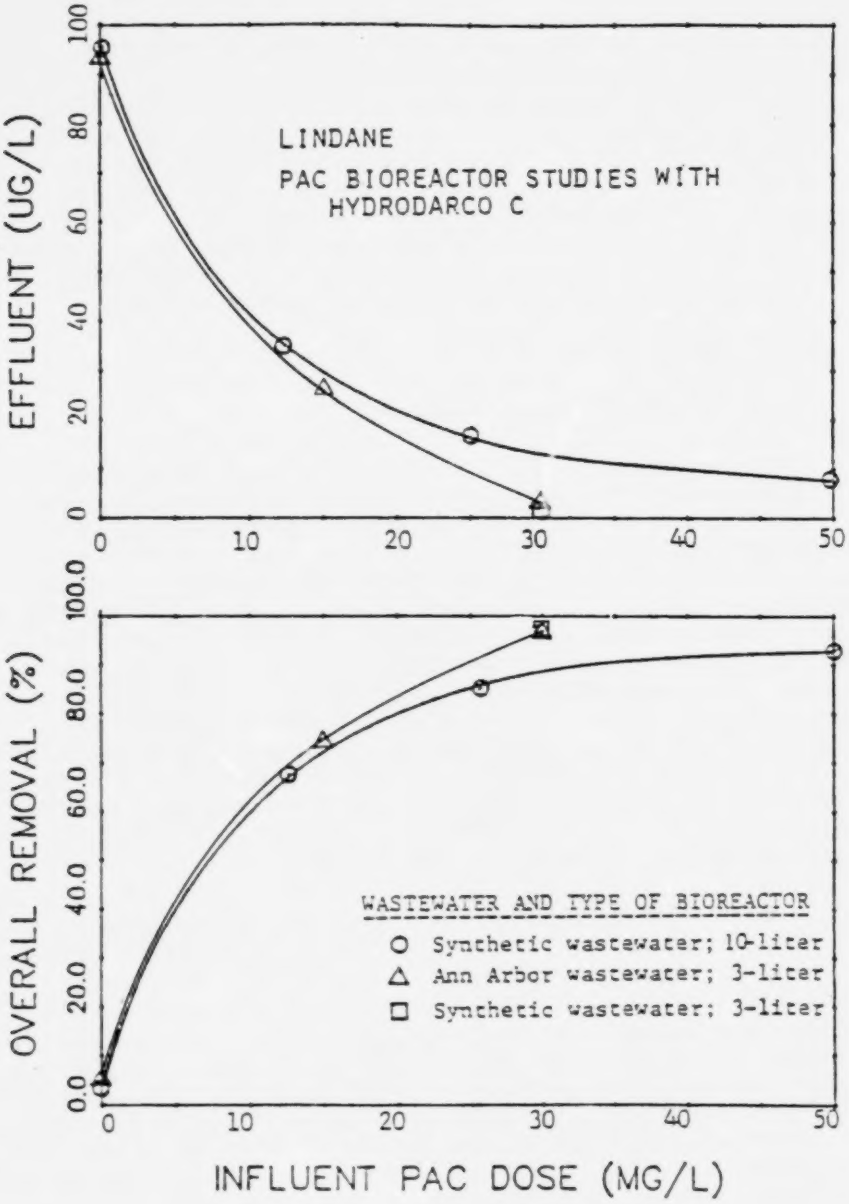


FIGURE 11-26. Effect of influent Hydrodarco C dose on lindane effluent concentration and overall removal measured during PAC-bioreactor studies with 3-liter and 10-liter bioreactors.

The removal of lindane was significantly better in the 3-liter bioreactors than in the 10-liter units as shown by the results plotted in Figure 11-26. Greater than 95% lindane removal was achieved in the smaller units at an influent Hydrodarco C dose of 30 mg/ℓ while 50 mg/ℓ Hydrodarco effected a 92% reduction in the 10-liter unit. In an effort to determine the reason for the differences in performance, a 3-liter bioreactor was operated with synthetic wastewater and a 30 mg/ℓ Hydrodarco C influent dose. There was no difference in performance between 3-liter bioreactors operated with synthetic wastewater and 3-liter bioreactors operated with Ann Arbor primary effluent. Average lindane removals were 96 and 96% for reactors with Ann Arbor primary effluent and synthetic wastewater, respectively. Differences in the nature and composition of the wastewater did not affect lindane removal by the powdered activated carbon.

11.4.2. Volatile Compounds

11.4.2.1. 1,2,4-Trichlorobenzene

The effect of PAC addition on the overall removal of 1,2,4-trichlorobenzene was evaluated at influent Hydrodarco C doses of 25, 50, 100 and 200 mg/ℓ in bioreactors operated with 6-day solids retention times. A summary of pertinent reactor conditions is outlined in Table 11-1. Bioreactor influents were composed of the synthetic wastewater detailed in Section 5-3, a 1,2,4-trichlorobenzene solution, and either slurried PAC or tap water. Results from the 25, 50, and 100 mg/ℓ PAC bioreactor studies have been compared to results from control activated sludge studies in Figures 11-27, 11-28, and 11-29, respectively. Influent, effluent, and off-gas concentrations for each study are shown along with N/N_0 values representing the fraction of the influent mass fluxes measured leaving the bioreactors in effluents and off-gases combined. The addition of 1,2,4-trichlorobenzene and slurried PAC to the influents was begun on Day Zero in each study represented by Figures 11-27 through 11-29.

The addition of 25 mg/ℓ PAC to the influent effected significant reductions in both effluent and off-gas 1,2,4-trichlorobenzene concentrations. Adsorption of 1,2,4-trichlorobenzene by the PAC effected reductions in effluent and off-gas concentrations of 72 and 69%, respectively. As shown by Figure 11-27, the mean effluent concentration was reduced from 12.0 to 3.3 μg/ℓ, and the mean off-gas value dropped from approximately 706 to 226 ng/ℓ for average influent 1,2,4-trichlorobenzene concentrations of 113 μg/ℓ. The fractional recovery of 1,2,4-trichlorobenzene averaged 0.31 in the 25 mg/ℓ PAC bioreactor indicating that the addition of 25 μg/ℓ PAC to the influent effected an overall removal of approximately 70%.

Effluent and off-gas concentrations were reduced further by the addition of 50 mg/ℓ PAC, as shown by the results given in Figure 11-28. The overall 1,2,4-trichlorobenzene removal averaged 77% during the seven week 50 mg/ℓ PAC bioreactor study. Mean effluent and off-gas

TABLE 11-6

LINDANE REMOVAL IN 3-LITER BIOREACTORS RECEIVING ANN ARBOR PRIMARY EFFLUENT

Influent PAC Dose	Influent Concentration (μg/ℓ)	Effluent Concentration (μg/ℓ)	Removal (%)
15 mg/ℓ Hydrodarco C	100 ± 20	27 ± 3	73
30 mg/ℓ Hydrodarco C	100 ± 20	4 ± 2	96
30 mg/ℓ SA-15	100 ± 20	4 ± 2	96
15 mg/ℓ PX-21	100 ± 20	2 ± 1	98
30 mg/ℓ PX-21	100 ± 20	2 ± 1	98

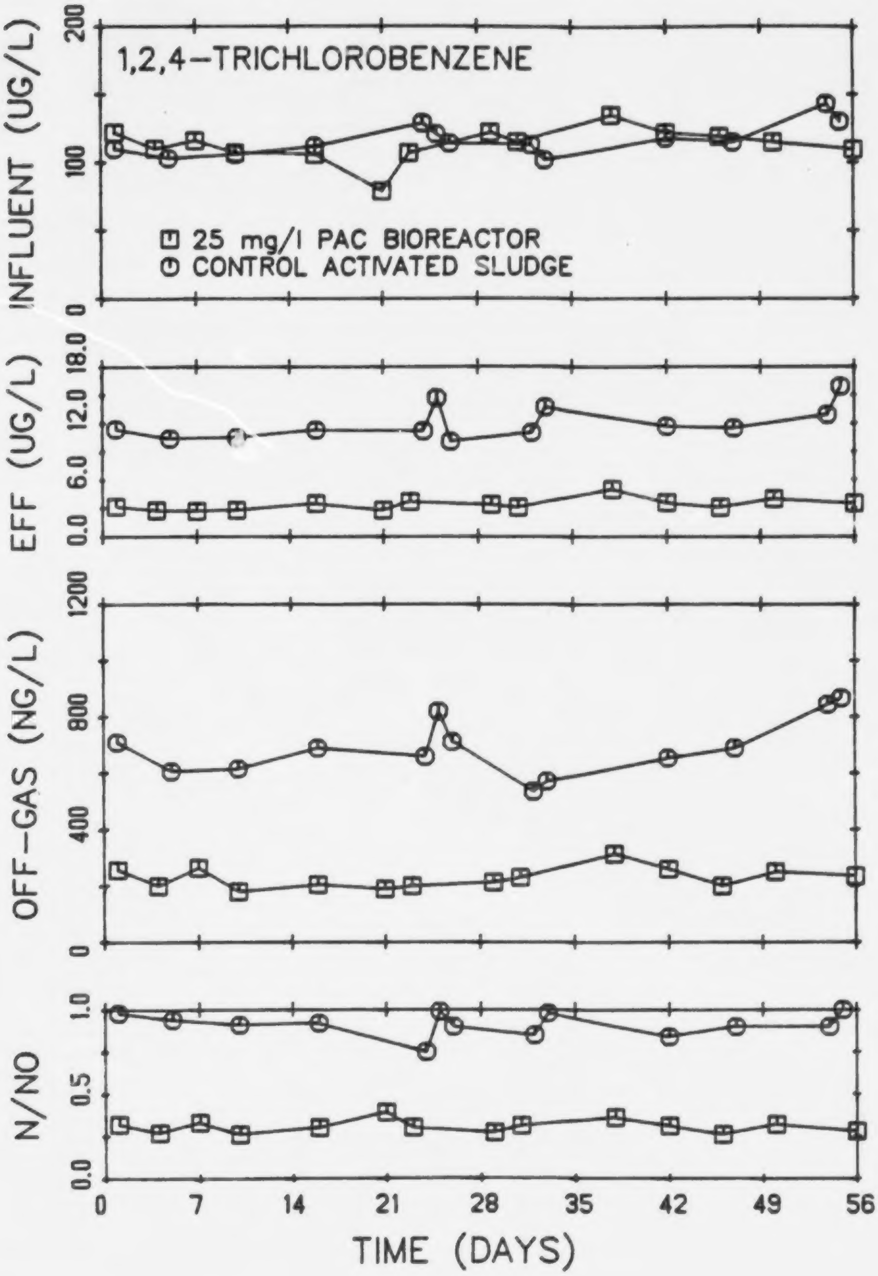


FIGURE 11-27. Effect of a 25 mg/l influent PAC dose on 1,2,4-trichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

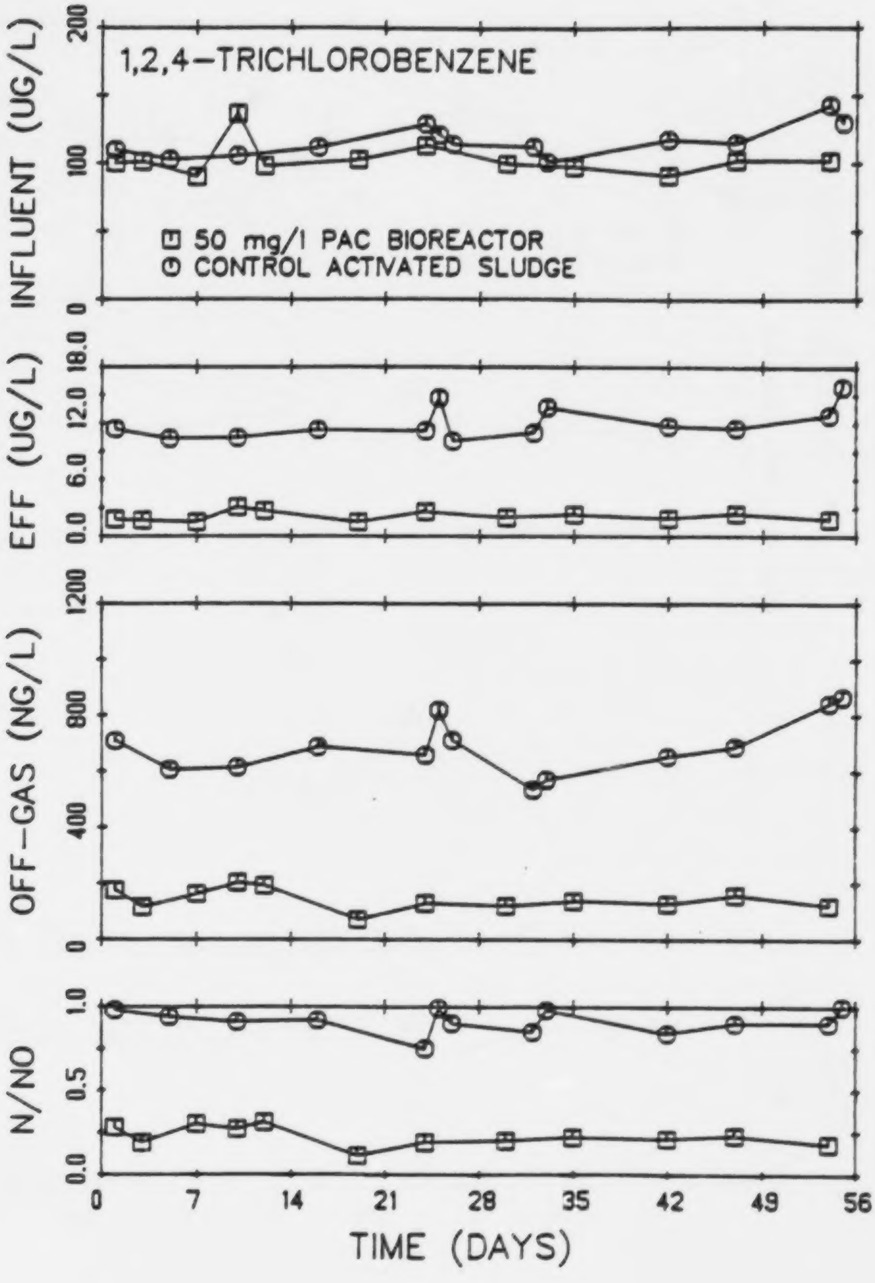


FIGURE 11-28. Effect of a 50 mg/l influent PAC dose on 1,2,4-trichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

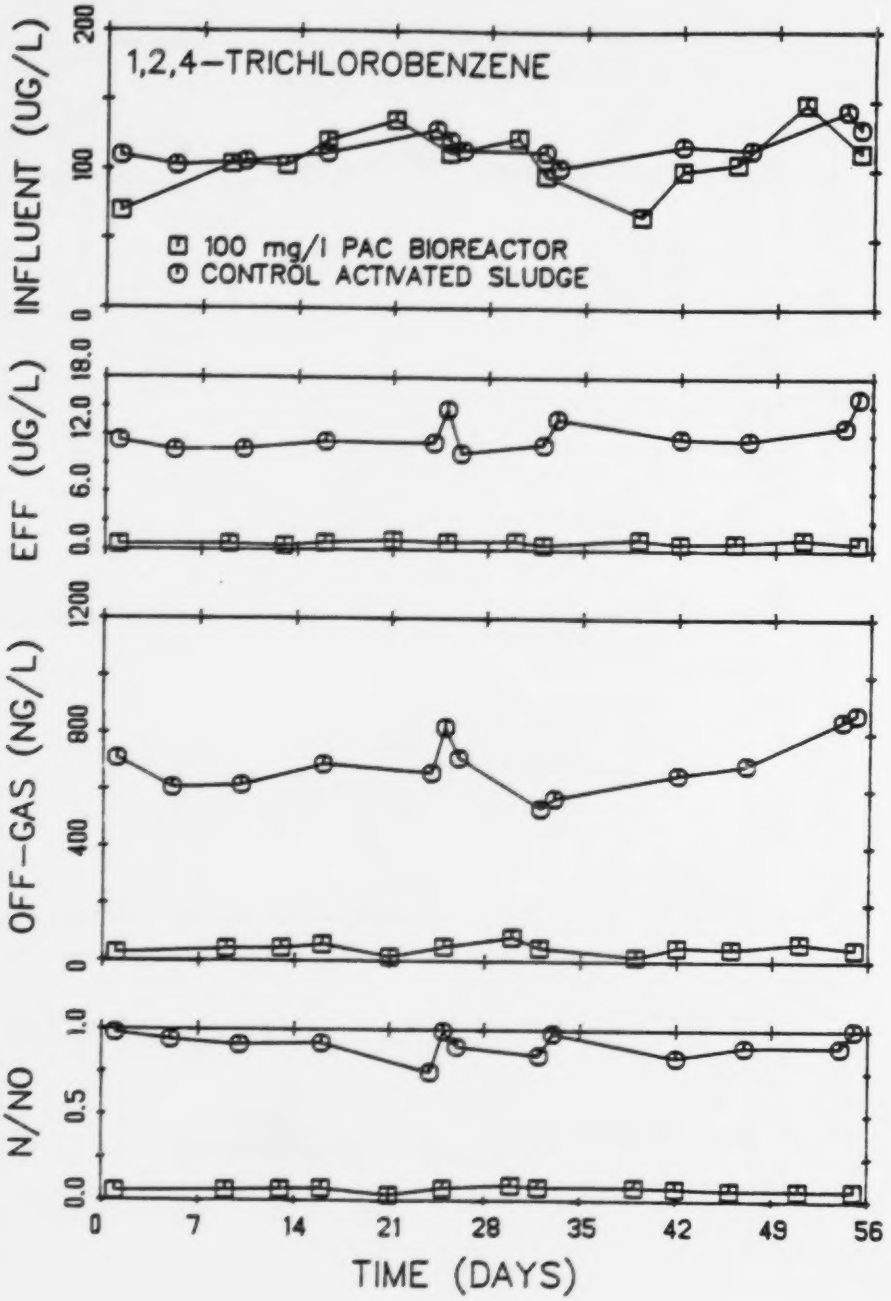


FIGURE 11-29. Effect of a 100 mg/l influent PAC dose on 1,2,4-trichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

concentrations were 2.1 μg/ℓ and 145 ng/ℓ, respectively, compared to values of 12 μg/ℓ and 706 ng/ℓ observed in the control unit. The influent concentration averaged 103 μg/ℓ. Adsorption of 1,2,4-trichlorobenzene by the PAC in the 50 mg/ℓ bioreactor effected percent reductions in effluent and off-gas concentrations that were approximately the same and averaged 80 and 77%, respectively. Figures 11-30 and 11-31 provide indication of relative effects of PAC addition and biodegradation on the removal of a volatile non-biodegradable compound, 1,2,4-trichlorobenzene, and a volatile biodegradable compound, benzene. A comparison of performance suggests that a PAC dose between 50 mg/ℓ and 100 mg/ℓ is required to effect a comparable overall removal of the biologically resistant 1,2,4-trichlorobenzene.

Influent PAC concentrations of 100 mg/ℓ produced overall 1,2,4-trichlorobenzene removals in excess of 90%, as shown by results from the 100 mg/ℓ PAC bioreactor study in Figure 11-29. The influent concentration averaged 109 μg/ℓ during the eight-week study while effluent and off-gas concentrations averaged 0.7 μg/ℓ and 43 ng/ℓ, respectively. Reductions in effluent and off-gas concentrations both averaged nearly 94% when measured values were compared to concentrations predicted to occur by the air-stripping model if no PAC was added to the bioreactor. Of the total flux of non-adsorbed 1,2,4-trichlorobenzene out of the 100 mg/ℓ PAC bioreactor, the distribution between the effluent and off-gas was similar to that observed in the control activated sludge unit with approximately 10% in the effluent and 90% in the off-gas.

Overall 1,2,4-trichlorobenzene removals calculated from the N/N_0 values presented in Figures 11-27 through 11-29 have been plotted in Figure 11-32. Overall removal increased with increasing influent PAC concentration over the range of 25 to 100 mg/ℓ. An influent PAC concentration of 25 mg/ℓ produced overall removals of nearly 70% while 100 mg/ℓ effected overall removals of approximately 95%. Overall removal has been defined as $(1-N/N_0)x100$ and includes reductions in the mass flux out of the bioreactor in effluents and off-gases combined. Although not shown in Figure 11-32, the addition of 200 mg/ℓ PAC to the influent produced approximately the same results as the 100 mg/ℓ dose.

Complete summaries of results from control and 25, 50, 100 and 200 mg/ℓ PAC bioreactor studies are given by Table 11-7. Table 11-7 presents influent, effluent and off-gas concentrations and overall removals predicted from measured effluent concentrations by Equations 10-11 and 10-12. In general, this method which does not require off-gas analyses to facilitate a mass balance provided accurate estimates of off-gas concentrations and overall 1,2,4-trichlorobenzene removals due to PAC adsorption. Similar findings were demonstrated for activated sludge bioreactors in Section 10.

Table 11-8 summarizes the fate of 1,2,4-trichlorobenzene in each PAC bioreactor study by comparing the amount leaving the bioreactors in effluents and off-gases to the amount adsorbed by the activated carbon. The amount adsorbed in each case was calculated from a reactor mass balance approach and not measured by extracting the PAC in the waste

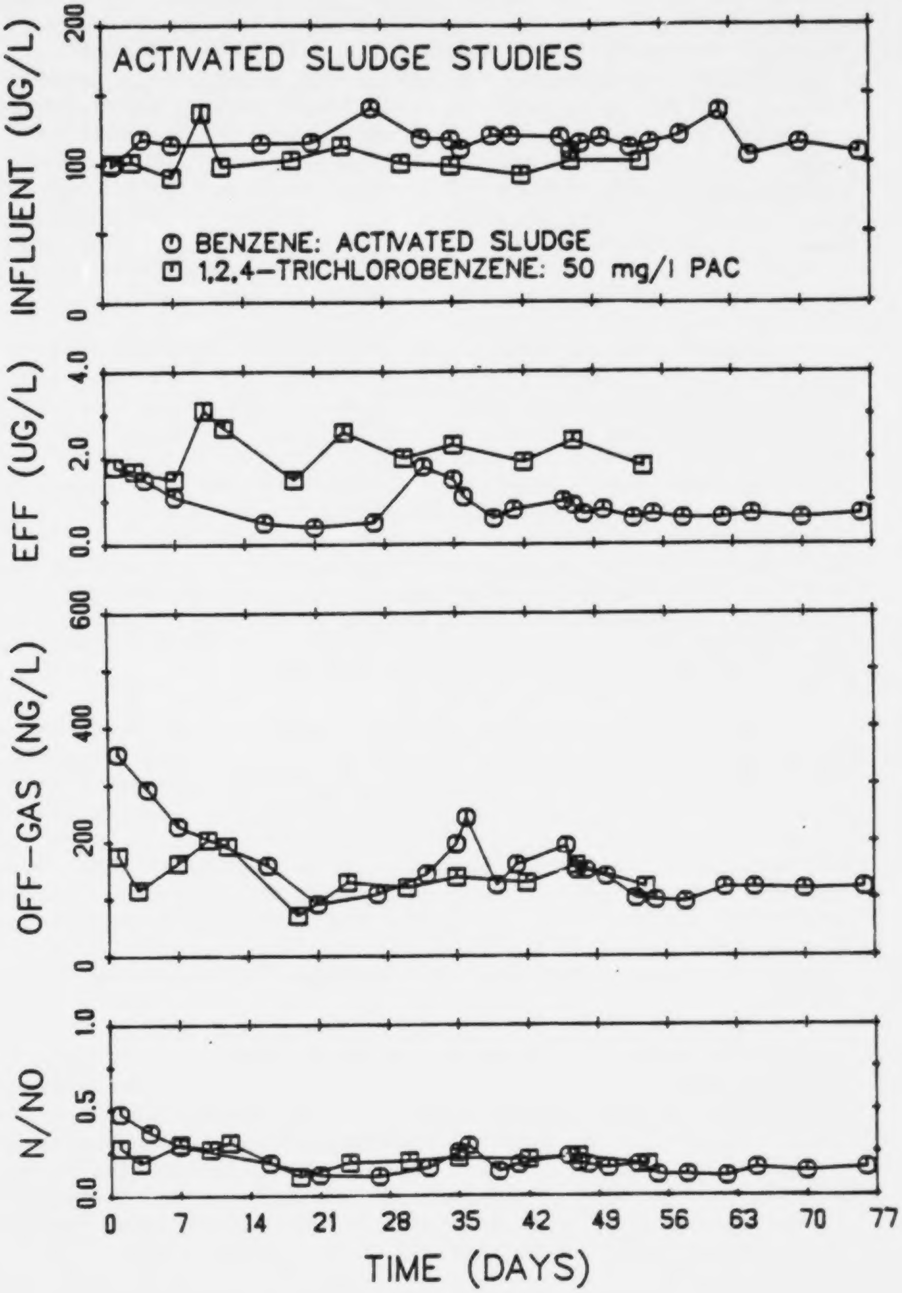


FIGURE 11-30. Comparison of effluent and off-gas concentrations and fractional recoveries, N/No, from a benzene control activated sludge study and a 1,2,4-trichlorobenzene PAC-bioreactor study with an influent PAC dose of 50 mg/l.

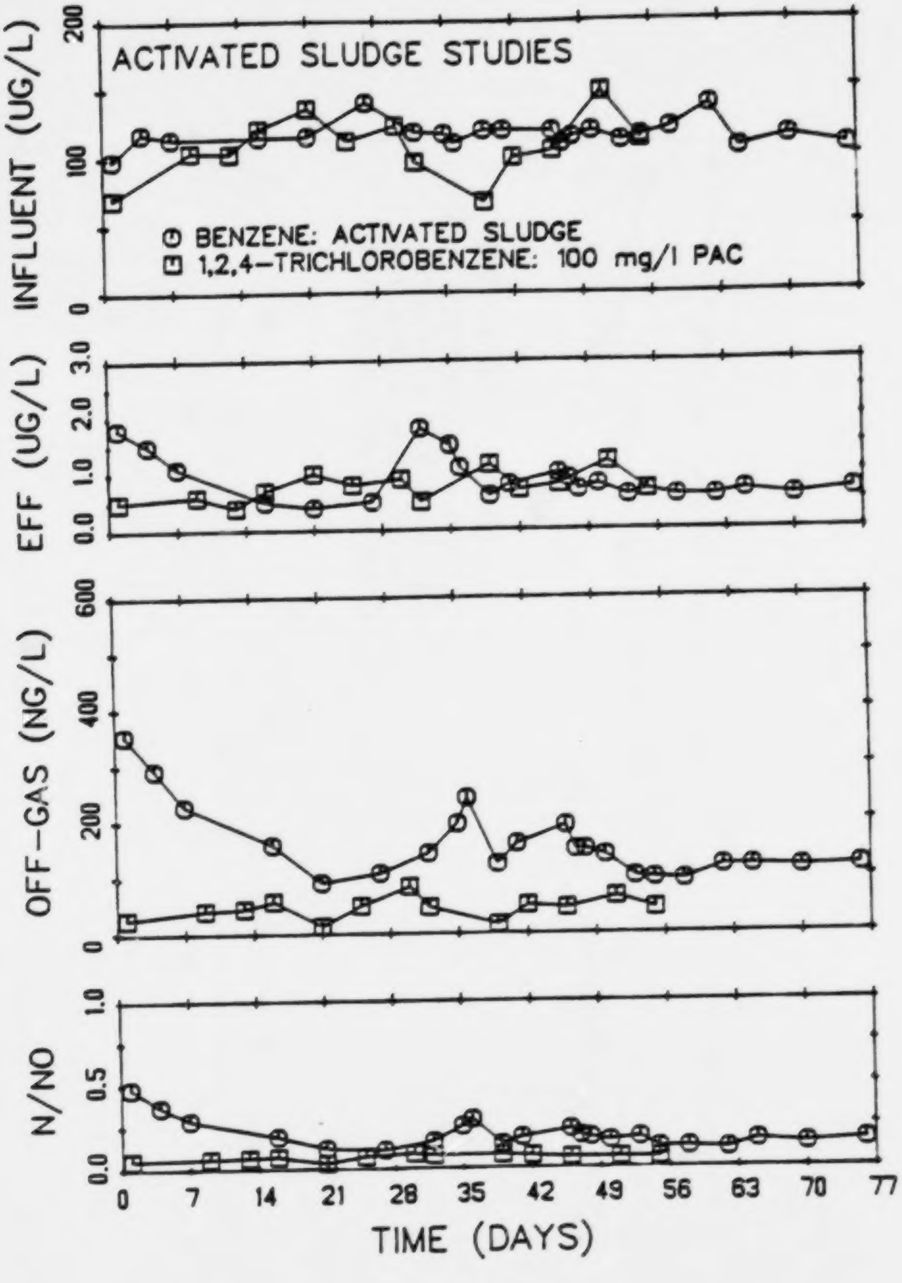


FIGURE 11-31. Comparison of effluent and off-gas concentrations and fractional recoveries, N/No, from a benzene control activated sludge study and a 1,2,4-trichlorobenzene PAC-bioreactor study with an influent PAC dose of 100 mg/l.

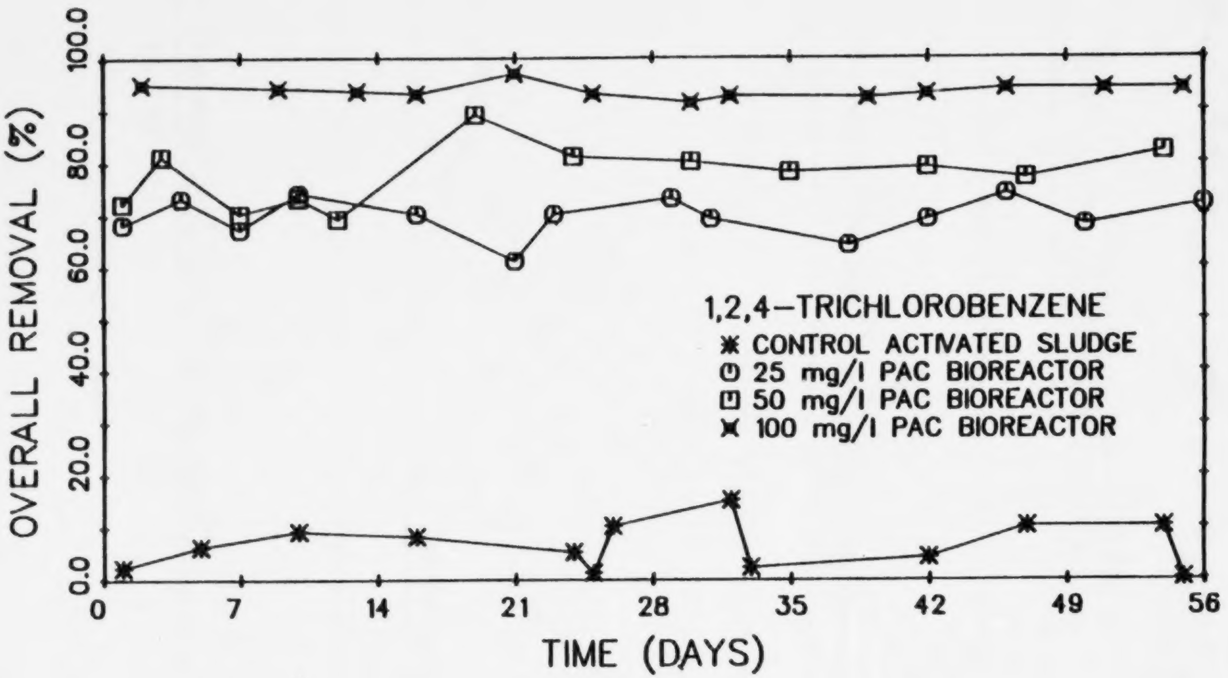


FIGURE 11-32. Comparison of 1,2,4-trichlorobenzene overall removals measured during a control activated sludge study and PAC-bioreactor studies with influent PAC doses of 25, 50, and 100 mg/l of Hydrodarco C.

TABLE 11-7

EFFECT OF INFLUENT PAC DOSE ON EFFLUENT AND OFF-GAS 1,2,4-TRICHLOROBENZENE CONCENTRATIONS

PAC Dose (mg/ℓ)	Influent (μg/ℓ)		Effluent (μg/ℓ)		Off-Gas (ng/ℓ)		N/N_o		Overall Removal (%)
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	
MEASURED									
Control	117	11.8	12.0	1.8	706	112	0.94	0.05	6
25	113	13.7	3.3	0.6	226	40	0.31	0.04	69
50	103	12.6	2.1	0.5	145	39	0.23	0.06	77
100	109	22.7	0.7	0.2	43	18	0.06	0.02	94
200	106	8.2	0.6	0.2	44	14	0.06	0.01	94
PREDICTED FROM EFFLUENT									
Control					756		0.99		1
25					208		0.28		72
50					132		0.20		80
100					44		0.06		94
200					38		0.06		94

TABLE 11-8

EFFECT OF PAC DOSE ON THE FATE OF 1,2,4-TRICHLOROBENZENE
DURING PAC/ACTIVATED SLUDGE TREATMENT

PAC Dose (mg/ℓ)	Percent of Influent Flux*			Percent of Non-adsorbed Flux Out of Bioreactor	
	Effluent	Off-Gas	Adsorbed	Effluent	Off-Gas
Control	10	90	<1	10	90
25	3	28	69	9	91
50	2	21	77	9	91
100	<1	6	94	11	89
200	<1	6	94	9	91

*Biodegradation assumed = 0%

sludge. Attempts to extract the PAC yielded incomplete and highly variable recoveries; therefore, data obtained from the extractions were not used in mass balance formulations. Table 11-8 also provides a comparison of the distribution between effluents and off-gases of the non-adsorbed 1,2,4-trichlorobenzene flux out of the bioreactors. In each bioreactor study, including the control activated sludge unit, approximately 90% of the non-adsorbed 1,2,4-trichlorobenzene left the units in the off-gases and only 10% left in the effluents. As shown in Table 11-8, this ratio was constant and not affected by the PAC dose.

Results summarized by Table 11-8 show that adsorption onto the activated carbon effected approximately the same percent reduction in effluent and off-gas concentrations at a given influent PAC dose. Percent reductions were calculated by comparing measured values to concentrations predicted to occur in a control activated sludge unit receiving the identical influent 1,2,4-trichlorobenzene concentrations and operated under identical operating conditions. Equations 10-11 and 10-12 were used to predict effluent and off-gas concentrations which essentially represented steady-state partitioning of 1,2,4-trichlorobenzene between the two phases.

The effect of increasing the PAC dose to a given bioreactor on the removal of 1,2,4-trichlorobenzene was examined in the bioreactor receiving the smallest PAC dose, 25 mg/ℓ. On Day 62 of the 25 mg/ℓ PAC bioreactor study the influent PAC dose was increased from 25 to 200 mg/ℓ by adjusting the concentration of the slurried PAC feed solution. Results from Day 42 through Day 96, presented in Figure 11-33, show the effect of increasing the influent PAC concentration. The increase in influent PAC dose produced an immediate decrease in steady-state effluent and off-gas concentrations. Within 24 hours effluent and off-gas concentrations decreased to approximately 0.5 µg/ℓ and 60 ng/ℓ, respectively. Approximately four weeks were required for the mixed liquor PAC concentration to increase from 500 to 600 mg/ℓ to a new steady-state level of 4400 to 5000 mg/ℓ. The increase in 1,2,4-trichlorobenzene removal was a function of influent PAC dose and not mixed liquor PAC concentration.

The 25/200 mg/ℓ PAC bioreactor study was used to examine the effect of spike influent 1,2,4-trichlorobenzene concentrations on effluent and off-gas concentrations and overall removals. During the 25 mg/ℓ PAC dose portion of the study the influent concentration of 1,2,4-trichlorobenzene was approximately doubled on Day 58. Results shown by Figure 11-33 indicate that while the off-gas concentration increased, the effluent concentration remained unchanged. There was no significant variation in overall % removal on Day 58. The influent concentration during the 200 mg/ℓ PAC dose operating period was increased on two occasions, to 243 µg/ℓ on Day 68 and to nearly 290 µg/ℓ on Day 74. The increased 1,2,4-trichlorobenzene loading caused only a small increase in off-gas concentrations but had no effect on effluent concentrations. Since overall % removals remained essentially constant during the spike loading periods the mass (µg/min) of 1,2,4-trichlorobenzene adsorbed by the PAC increased with increasing

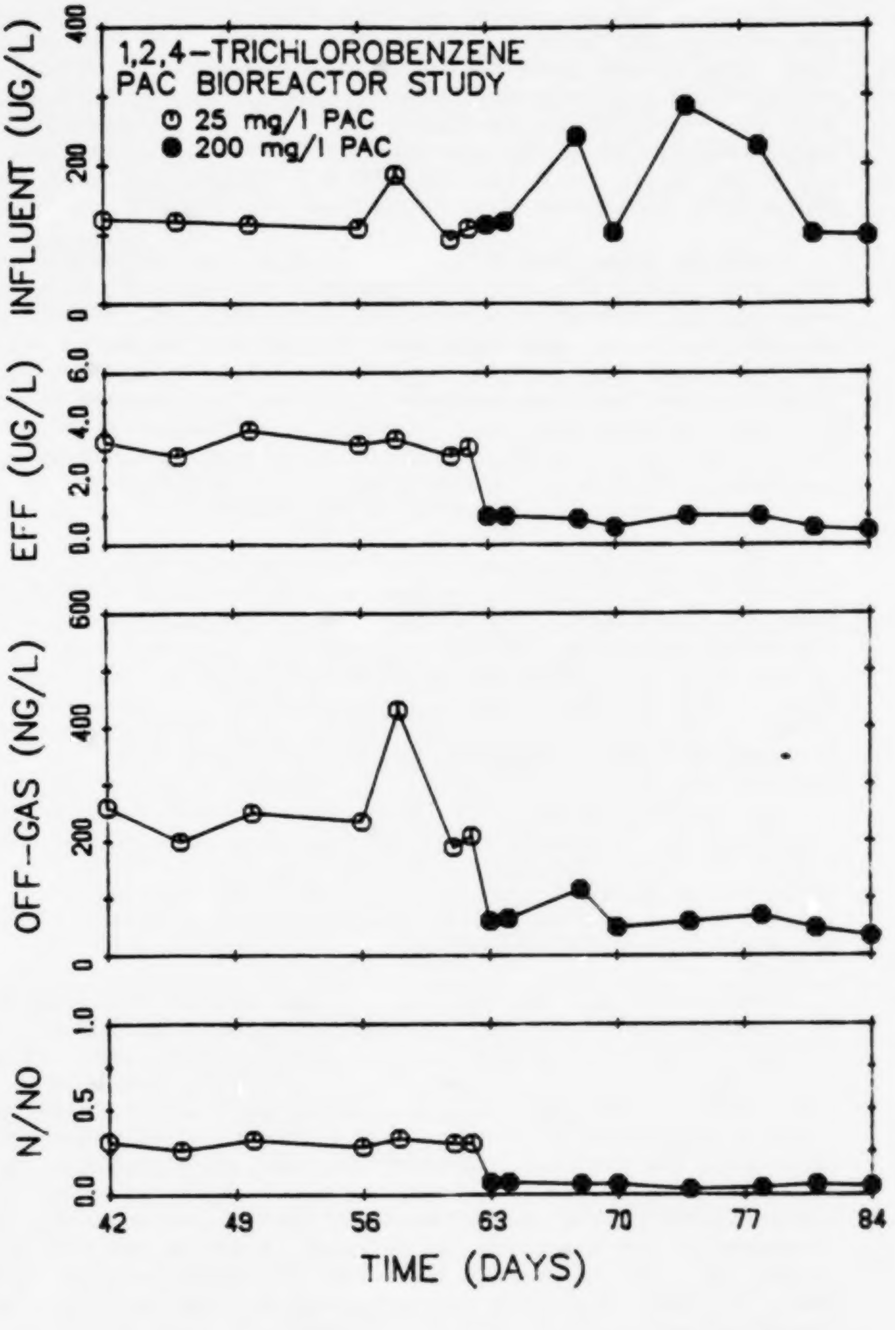


FIGURE 11-33. Effect of increasing the influent PAC dose from 25 to 200 mg/l on the 1,2,4-trichlorobenzene effluent and off-gas concentration and fractional recovery, N/No.

influent concentration. As shown by Figure 11-34, there was a linear relationship between the amount adsorbed and the influent 1,2,4-trichlorobenzene loading during both the 25 and 200 mg/ℓ doses. Slopes and regression coefficients which were forced through the origin were 0.69 and 0.999, respectively, for the 25 mg/ℓ PAC dose and 0.95 and 0.999, respectively for the 200 mg/ℓ dose. The amount of 1,2,4-trichlorobenzene adsorbed, measured in μg/min, was larger when the influent PAC dose was 200 mg/ℓ compared to 25 mg/ℓ as shown in Figure 11-34.

Steady-state data from the PAC studies (Table 11-7) was used to calculate the relationship plotted in Figure 11-35, which indicates less efficient adsorption of 1,2,4-trichlorobenzene with increasing dosage of PAC, consistent with results presented for lindane in Section 11.4.1.

11.4.2.2. 1,2-Dichlorobenzene

The effect of PAC addition to activated sludge reactors on the removal of 1,2-dichlorobenzene was evaluated at influent Hydrodarco C doses of 25, 50, 100 and 200 mg/ℓ in bioreactors operated with 6-day solids retention times. Results from the 25, 50, and 100 mg/ℓ PAC studies have been compared with results from control activated sludge studies in Figures 11-36 through 11-38, respectively. Each figure includes plots of influent, effluent, and off-gas concentrations along with N/N_0 values representing the fraction of influent mass fluxes leaving the bioreactors in effluents and off-gases combined. The addition of 1,2-dichlorobenzene and slurried PAC to the influents was begun on Day Zero in each study represented by Figures 11-36 to 11-38.

The addition of 25 mg/ℓ of Hydrodarco C to the influent produced measurable reductions in both effluent and off-gas concentrations compared to concentrations measured in a control activated sludge unit, as shown by Figure 11-36. The mean effluent and off-gas concentrations were reduced from 7.8 to 4.3 μg/ℓ and from 477 to 298 ng/ℓ, respectively. Mean influent concentrations in both control and 25 mg/ℓ PAC bioreactor studies were approximately 110 μg/ℓ. The addition of 25 mg/ℓ PAC to the influent effected an improvement in the overall 1,2-dichlorobenzene removal from the 36% observed in the control unit to 61%.

The overall removal of 1,2-dichlorobenzene averaged approximately 71% during eight weeks of steady-state operation in a 6-day SRT bioreactor receiving 50 mg/ℓ PAC. Mean effluent and off-gas concentrations during the eight week study were 2.9 μg/ℓ and 201 ng/ℓ, respectively. Percent reductions in effluent and off-gas concentrations during the 50 mg/ℓ PAC bioreactor study were similar and averaged 63 and 58%, respectively. Since the off-gas was the principal exit route of 1,2-dichlorobenzene out of the bioreactors, the reduction in mass flux measured in μg/min was significantly larger for the off-gas (1.10 μg/min) than the effluent (0.15). In general, the off-gas flux represented approximately 90% of the total non-adsorbed 1,2-dichlorobenzene flux out of the bioreactors while the effluent flux represented only 10%.

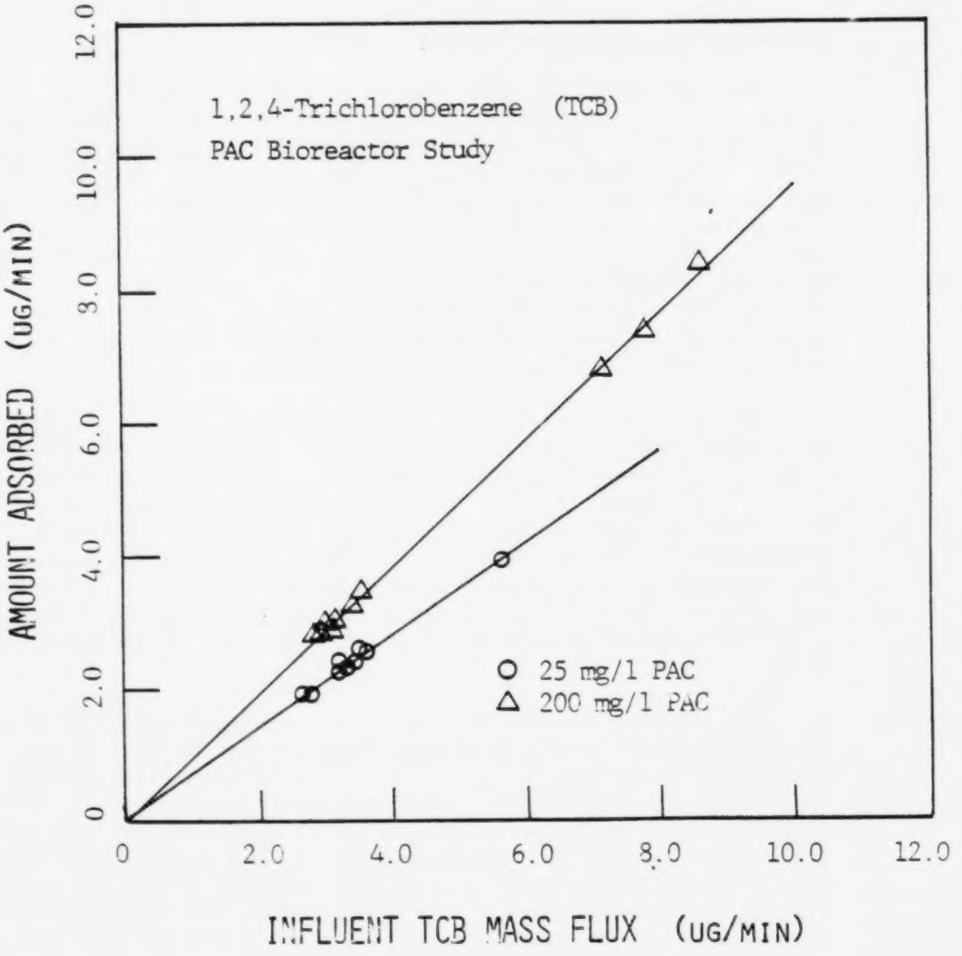


FIGURE 11-34. Relationship between the amount of 1,2,4-trichlorobenzene adsorbed by the PAC and the influent mass flux of 1,2,4-trichlorobenzene during the 25/200 mg/1 PAC bioreactor study.

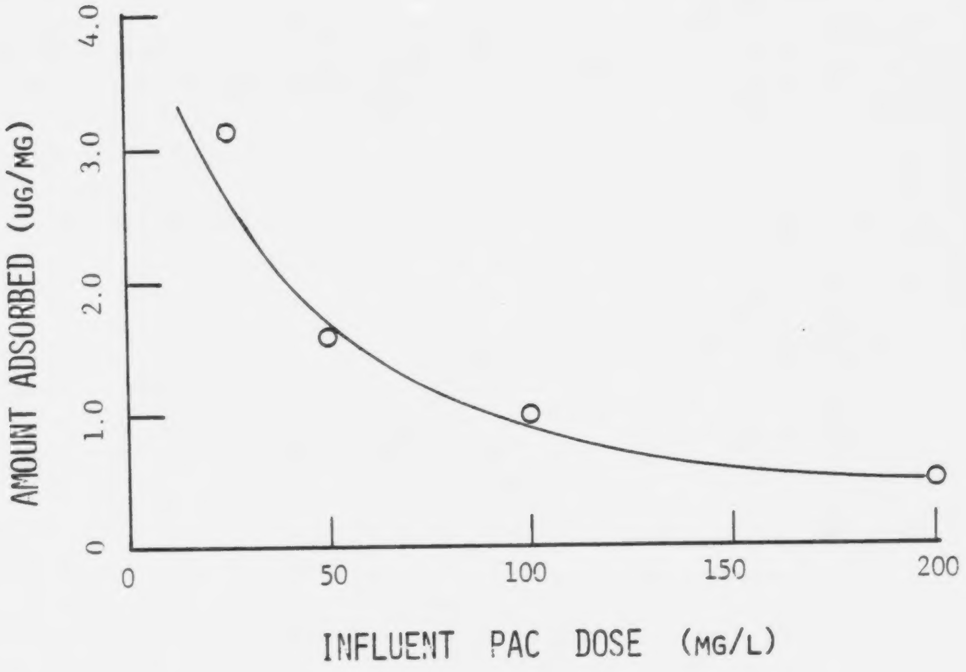


FIGURE 11-35. Effect of influent PAC dose on the amount of 1,2,4-trichlorobenzene adsorbed during PAC-bioreactor studies.

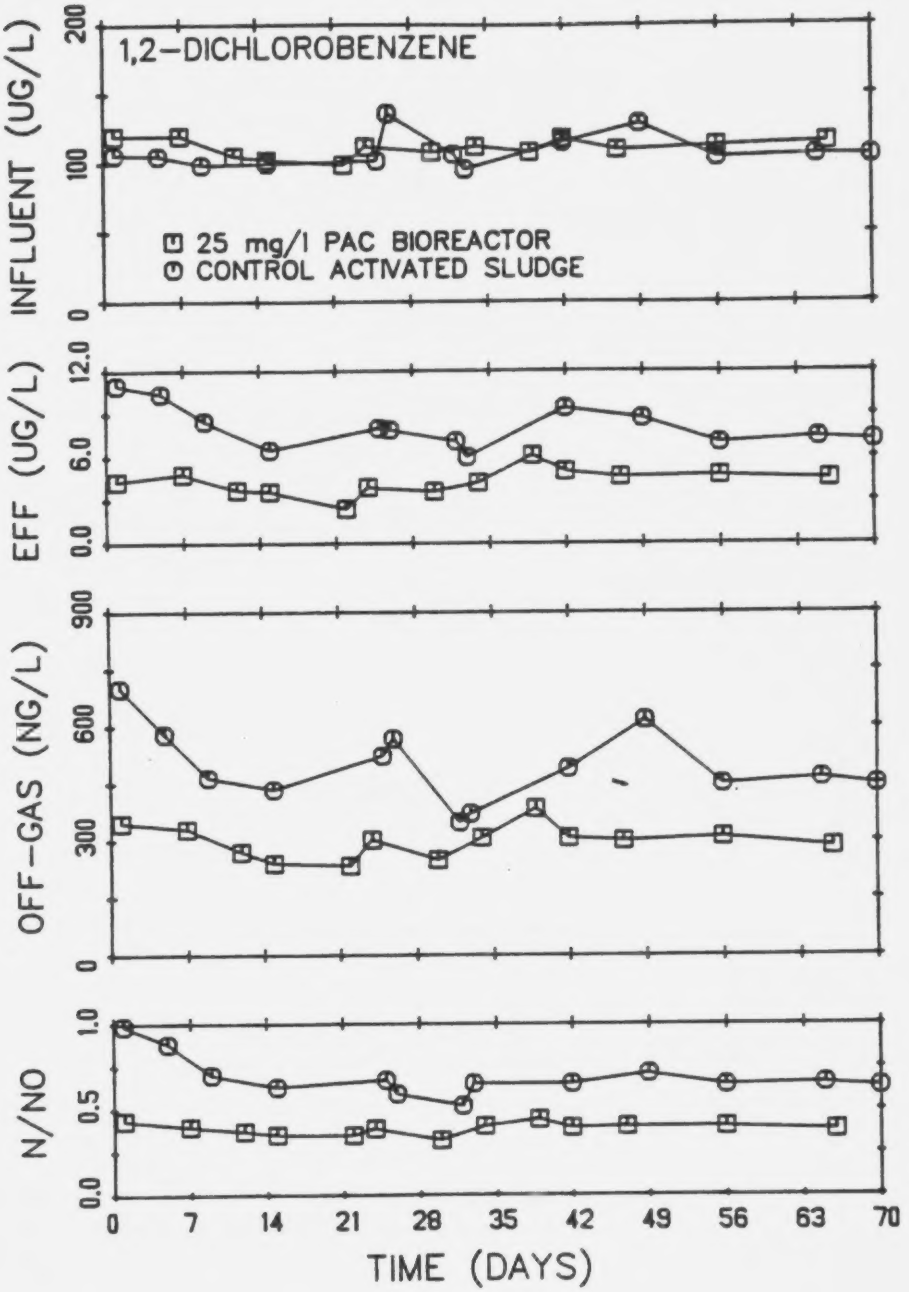


FIGURE 11-36. Effect of a 25 mg/l influent PAC dose on 1,2-dichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

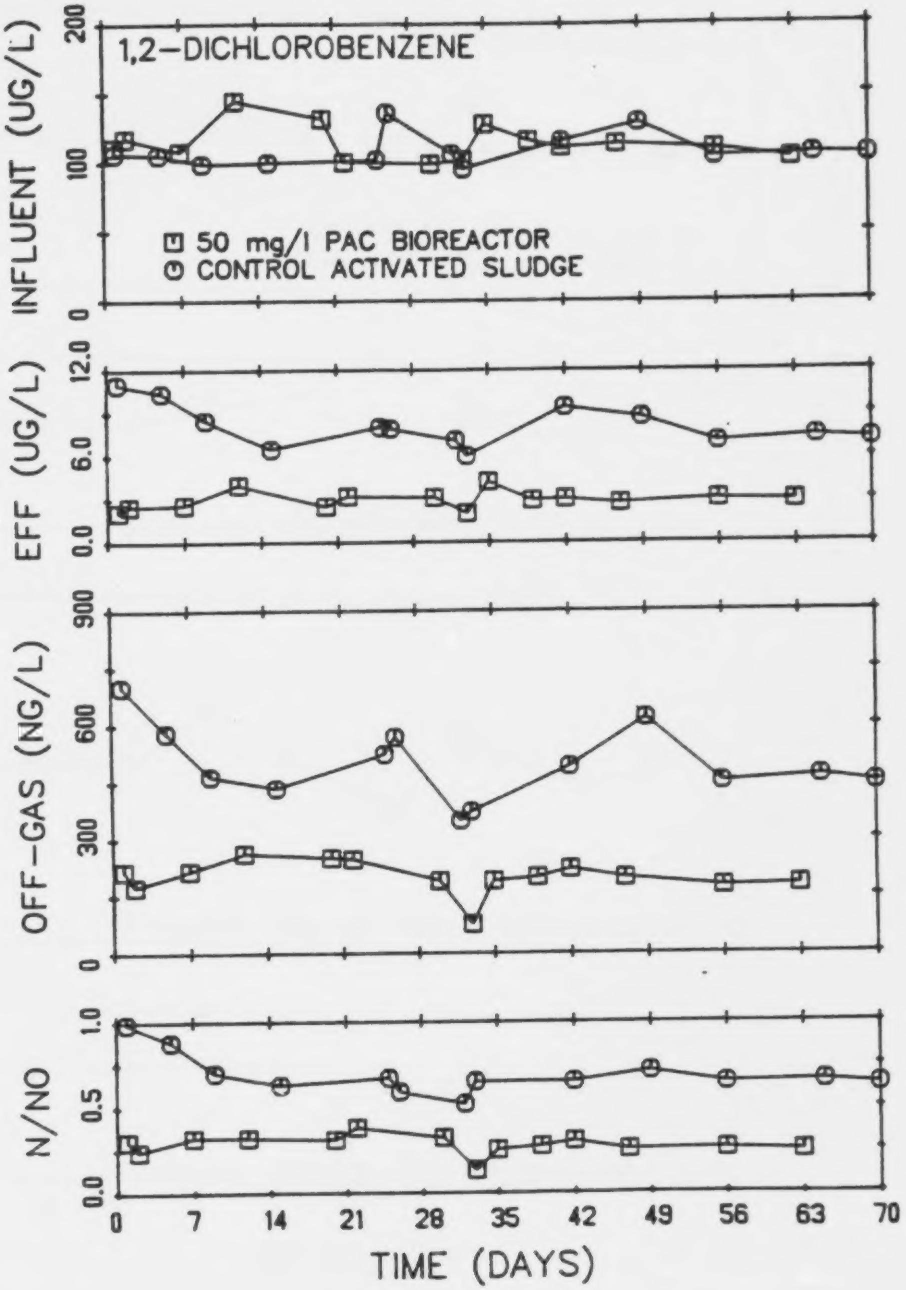


FIGURE 11-37. Effect of a 50 mg/l influent PAC dose on 1,2-dichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

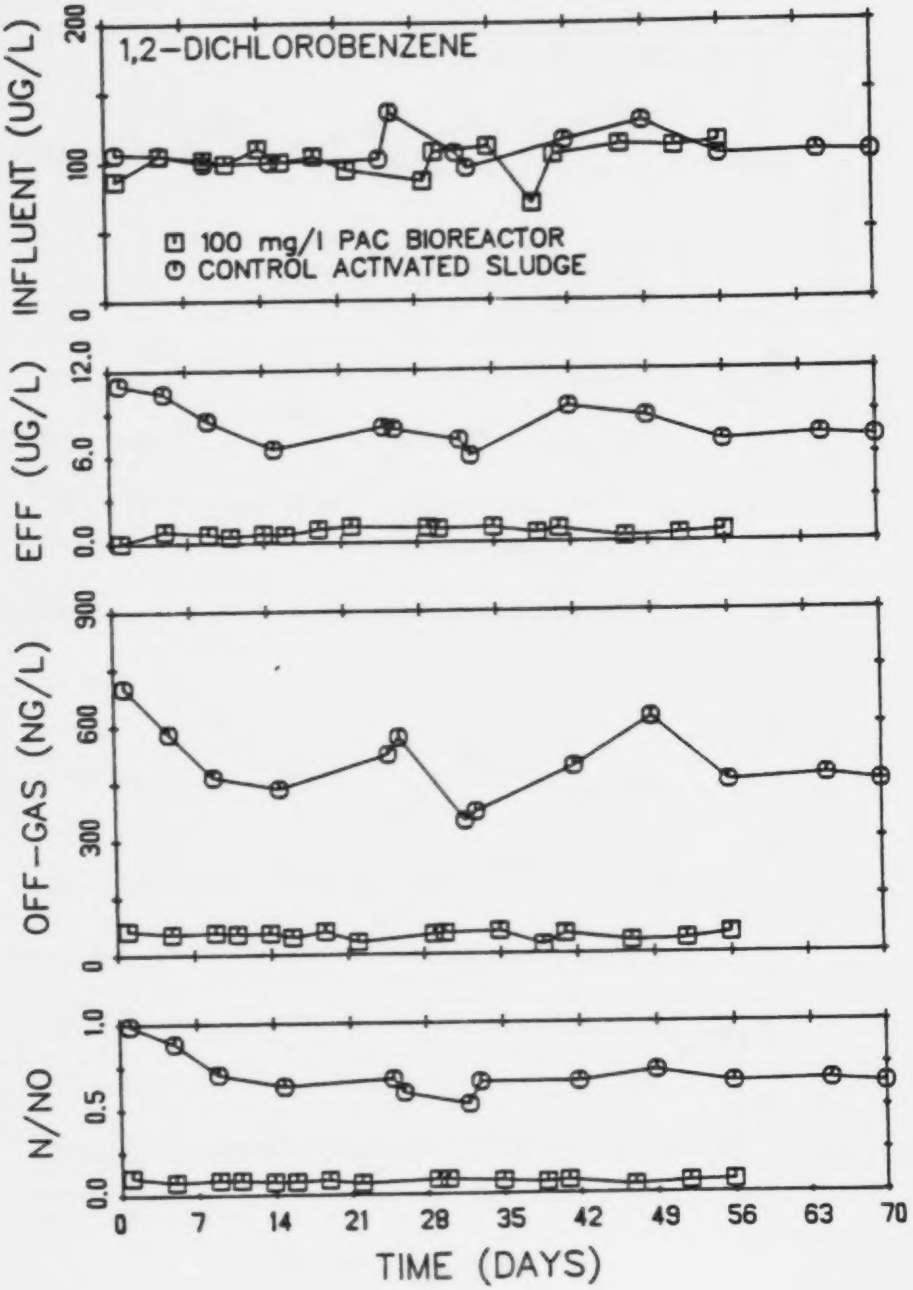


FIGURE 11-38. Effect of a 100 mg/l influent PAC dose on 1,2-dichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

Additional improvement in bioreactor performance with respect to 1,2-dichlorobenzene removal was accomplished with an influent PAC dose of 100 mg/ℓ. The overall removal averaged nearly 93% during the seven week 100 mg/ℓ PAC bioreactor study. Mean influent, effluent and off-gas concentrations were 94 μg/ℓ, 0.7 μg/ℓ, and 44 ng/ℓ, respectively. Compared to results from the control activated sludge unit, these concentrations represented reductions in effluent and off-gas concentrations in excess of 90% in each case.

The largest influent PAC dose examined was 200 mg/ℓ. Results from this bioreactor study were not significantly different from those observed in the 100 mg/ℓ PAC bioreactor study. The overall 1,2-dichlorobenzene removal averaged 94%. Mean effluent and off-gas concentrations of 0.6 μg/ℓ and 56 ng/ℓ, respectively, were approximately the same as measured in 100 mg/ℓ PAC dose study. The results indicated that there was no increased benefit from using a 200 mg/ℓ compared to a 100 mg/ℓ dose for relatively constant influent 1,2-dichlorobenzene concentrations used in the PAC bioreactor studies. A complete summary of results for 1,2-dichlorobenzene is given in Table 11-9.

The overall removals of 1,2-dichlorobenzene observed during the control activated sludge,25 mg/ℓ, 50 mg/ℓ, and 100 mg/ℓ PAC bioreactor studies have been compared in Figure 11-39. The incremental increase in overall removal decreased with increasing PAC dose such that there was no significant difference between results obtained from PAC reactors receiving influent doses of 100 and 200 mg/ℓ.

A significant feature of the results in Figures 11-36 through 11-39 was the immediate establishment of steady-state removals of 1,2-dichlorobenzene. While the control activated sludge unit experienced an acclimation period of 14 days prior to steady-state 1,2-dichlorobenzene removal, the PAC units reached steady-state removals within 24 hours after the addition of PAC to the influent.

The effect of increasing the influent PAC dose on the removal of 1,2-dichlorobenzene was studied in the 25 mg/ℓ PAC bioreactor previously described. After 63 days of operation with the initial 25 mg/ℓ PAC dose, the influent PAC concentration was increased to 200 mg/ℓ. Results in Figure 11-40 show that effluent and off-gas concentrations decreased to new steady-state levels within 24 hours after the change in influent PAC concentration.

During this study the effect of spike 1,2-dichlorobenzene loadings on effluent and off-gas concentrations and overall removals were evaluated. The first spike loading test was conducted during the 25 mg/ℓ influent PAC operating period. Effluent and off-gas concentrations increased on Day 52 in response to an increase in the influent concentration from 100 to nearly 400 μg/ℓ. While the overall 1,2-dichlorobenezene removal remained constant at 62%, the effluent concentration rose from 5 to 15 μg/ℓ.

The bioreactor was dosed with a second spike loading between Days 72 and 80 when the influent PAC dose was 200 mg/ℓ. Effluent and off-gas concentration increased only slightly as shown by Figure 11-40, even

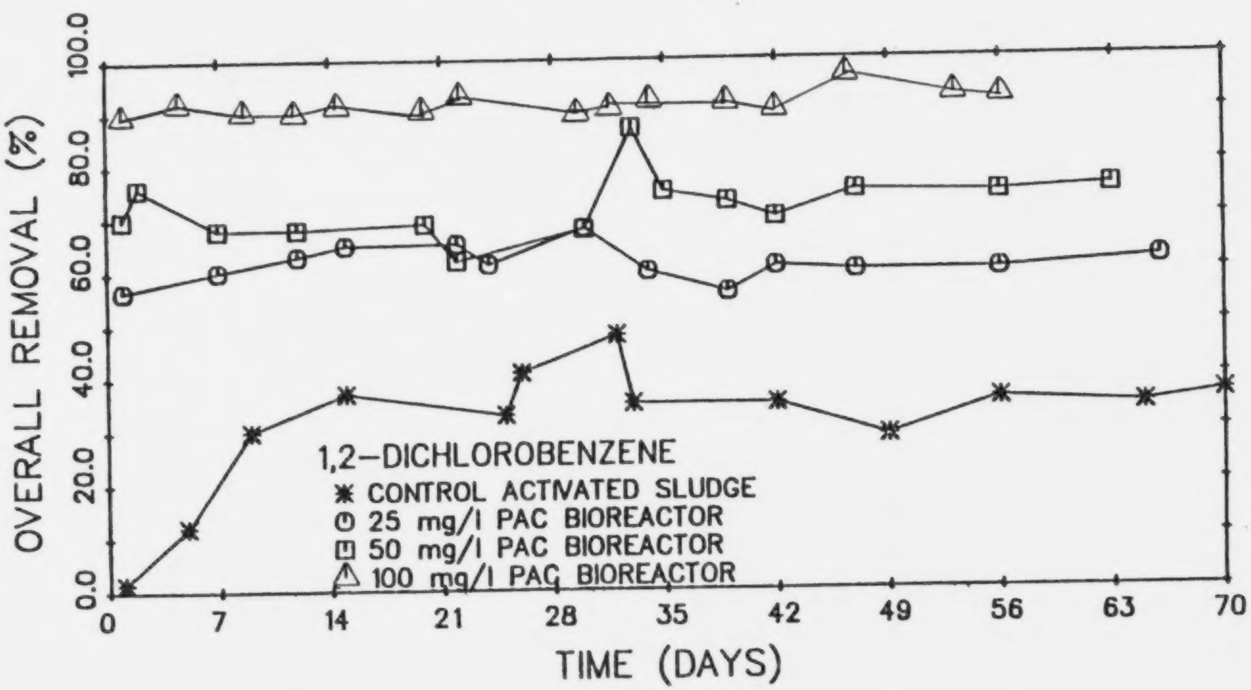


FIGURE 11-39. Comparison of 1,2-dichlorobenzene overall removals measured during a control activated sludge study and PAC-bioreactor studies with influent PAC doses of 25, 50, and 100 mg/l of Hydrodarco C.

TABLE 11-9

SUMMARY OF PAC BIOREACTOR RESULTS
FOR 1,2-DICHLOROBENZENE

PAC Dose (mg/ℓ)	Influent (μg/ℓ) Mean	Influent (μg/ℓ) S.D.	Effluent (μg/ℓ) Mean	Effluent (μg/ℓ) S.D.	Off-Gas (ng/ℓ) Mean	Off-Gas (ng/ℓ) S.D.	N/N_o Mean	N/N_o S.D.	Overall Removal (%)
MEASURED									
Control	110	13.3	7.8	1.2	477	93	0.64	0.05	36
25	111	6.6	4.3	0.9	298	44	0.39	0.04	61
50	115	13.1	2.9	0.6	201	46	0.29	0.06	71
100	94	28.0	0.7	0.2	44	16	0.07	0.01	93
200	118	10.0	0.6	0.2	58	17	0.06	0.01	94
PREDICTED FROM EFFLUENT									
Control					483		0.65		35
25					276		0.38		62
50					186		0.25		75
100					45		0.07		93
200					38		0.05		95

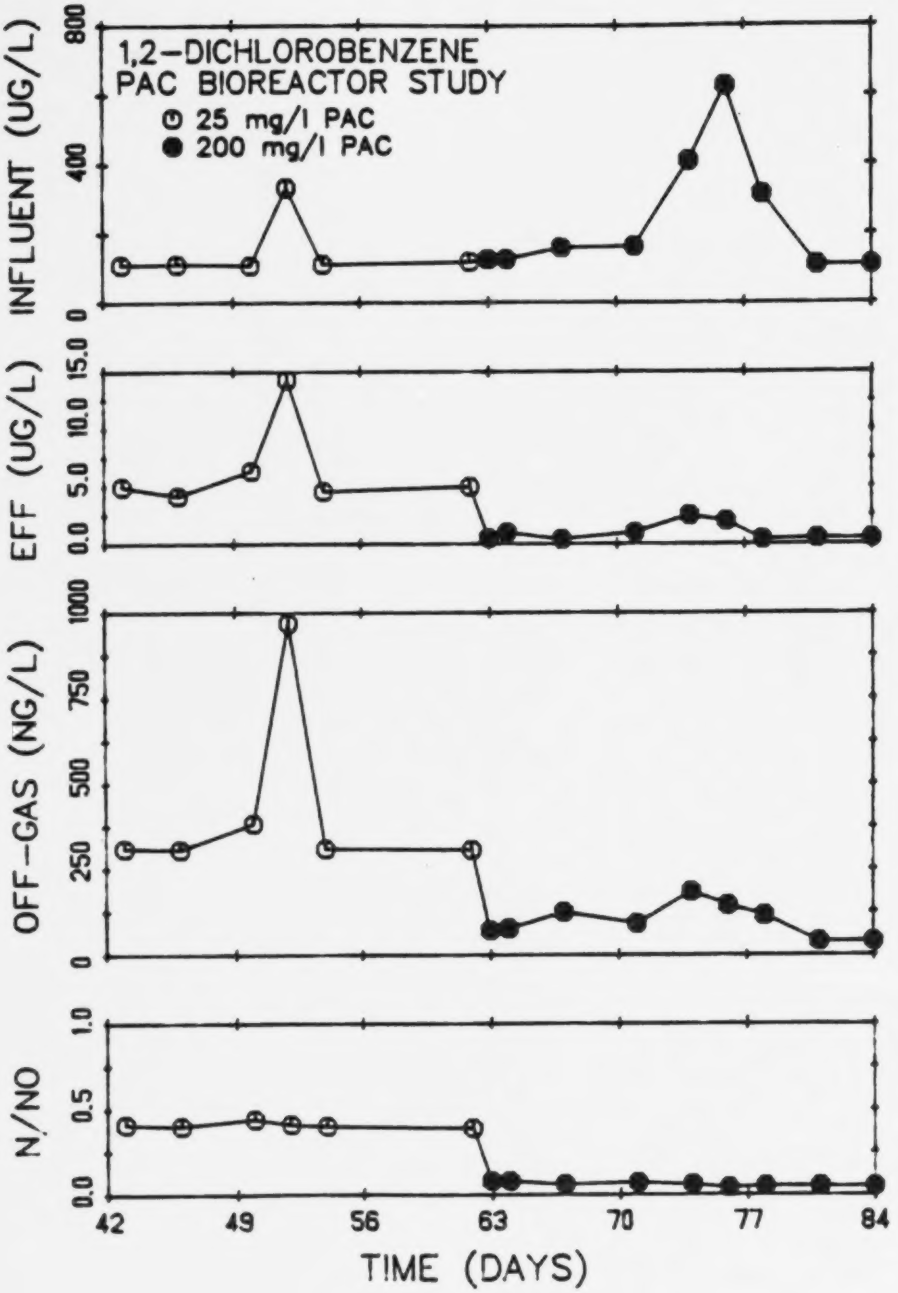


FIGURE 11-40. Effect of increasing the influent PAC dose from 25 to 200 mg/l on the 1,2-dichlorobenzene effluent and off-gas concentration and fractional recovery, N/No.

though the influent concentration rose to almost 700 μg/ℓ. The effluent and off-gas concentrations during this spike loading period were less than the values recorded for the steady-state operating period with a 25 mg/ℓ PAC dose. The 200 mg/ℓ PAC dose acted as a buffer in the system to dampen the effect of significant increases in the influent concentration on measured effluent and off-gas values.

11.5 REMOVAL OF BIODEGRADABLE COMPOUNDS

Powdered activated carbon/activated sludge bioreactor studies were conducted with the biodegradable compounds: benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, and nitrobenzene. Influent PAC concentrations ranging from 25 to 200 mg/ℓ were studied in bioreactors operated at a 6-day SRT.

There was a significant difference between the results from PAC/activated sludge bioreactor studies with the biodegradable compounds and those with the poorly and non-biodegradable compounds. While influent PAC doses of 25 mg/ℓ to 100 mg/ℓ produced significant improvements in overall removals of lindane, 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, compared to control bioreactors such influent PAC doses had little effect on the overall removals of the biodegradable compounds compared to removals measured in control activated sludge reactors.

11.5.1 Non-volatile Compound

Baseline volatilization studies and activated sludge bioreactor studies showed that nitrobenzene was a highly biodegradable compound of relatively low volatility. PAC bioreactor studies were conducted with influent PAC doses of 50 and 100 mg/ℓ Hydrodarco C, 50 mg/ℓ SA-15 and 50 mg/ℓ PX-21. The bioreactor studies were conducted under the operating conditions listed in Table 11-1 with a six day SRT.

Results from the 50 and 100 mg/ℓ PAC bioreactor studies with Hydrodarco C have been graphically compared to results from a control activated sludge unit in Figures 11-41 and 11-42, respectively. The effect of PAC addition can be divided into two categories: during the two-week acclimation phase and during the steady-state biodegradation phase. In each study, the effluent concentration from the unit receiving PAC reached approximate steady-state levels within 24 hours after both slurried PAC and nitrobenzene were initially added to the bioreactors. During the first two weeks the effluent nitrobenzene concentrations in the 50 and 100 mg/ℓ PAC units were significantly lower than observed in control activated sludge reactors, as shown by Figures 11-41 and 11-42. Once the control activated sludge bioreactors attained a steady-state level of nitrobenzene biodegradation, there was essentially no difference in nitrobenzene removal between the control and 50 mg/ℓ PAC bioreactors. The effluent concentration from the 100 mg/ℓ PAC bioreactor averaged slightly less than the control activated sludge unit. As shown by Figure 11-43, the effluent concentration of the 100 mg/ℓ PAC bioreactor was consistently less than that of the 50 mg/ℓ PAC bioreactor throughout the nine weeks of the studies. Complete summaries of the two studies have been presented in Table 11-10.

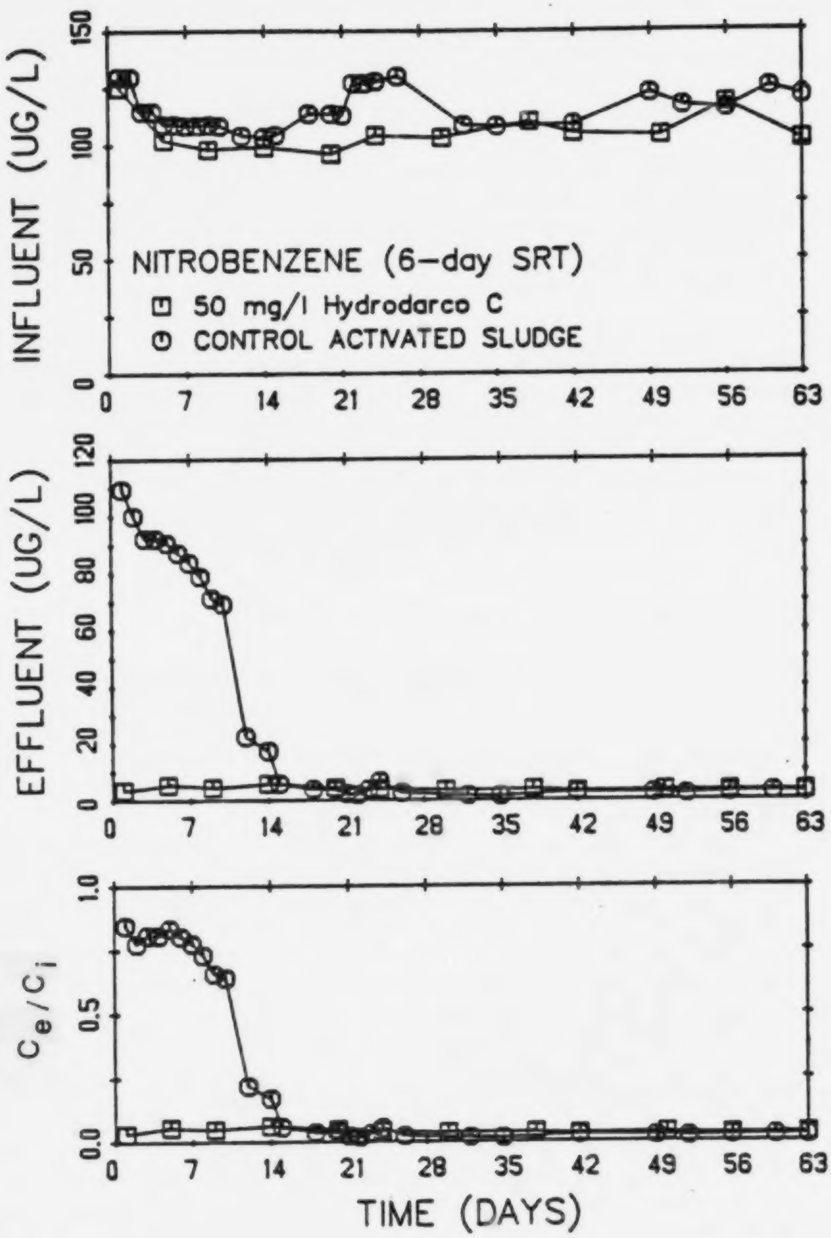


FIGURE 11-41. Effect of a 50 mg/l PAC concentration on the effluent nitrobenzene concentration.

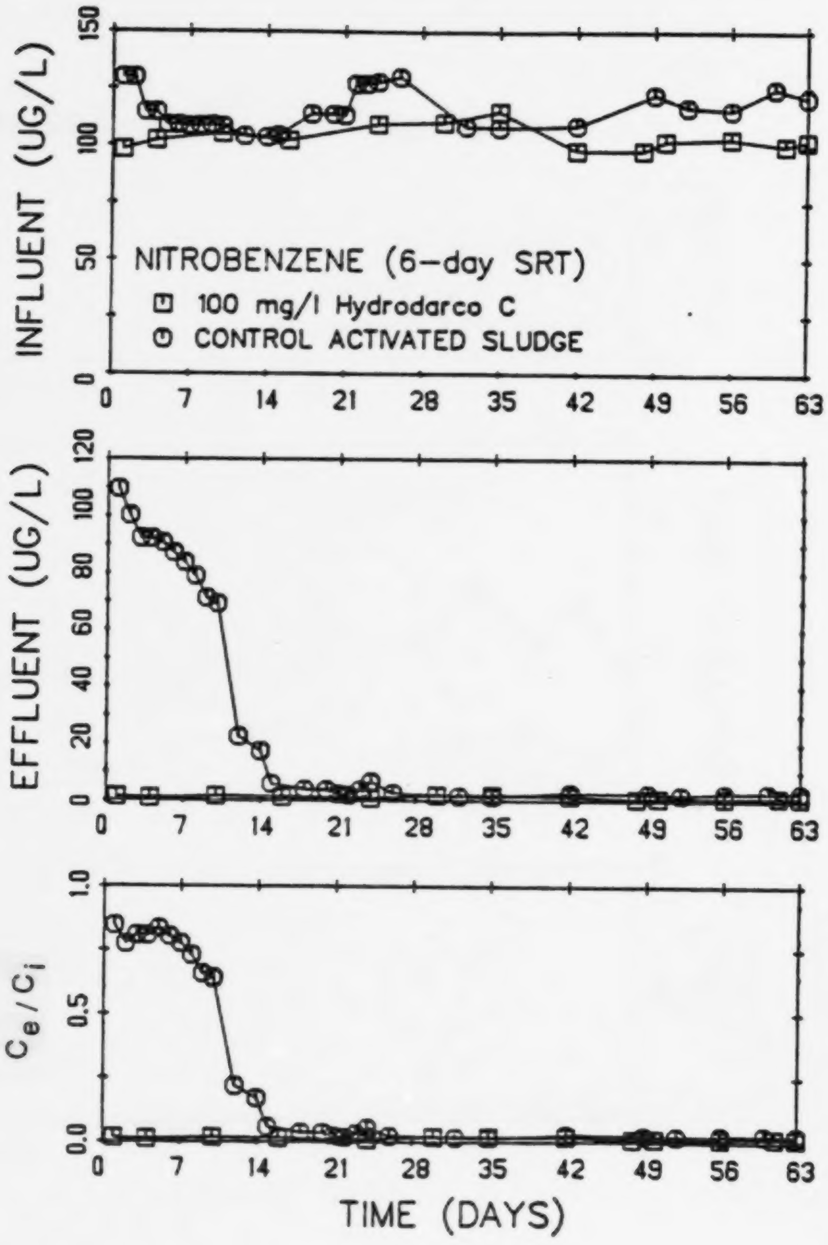


FIGURE 11-42. Effect of a 100 mg/l PAC influent concentration on the nitrobenzene effluent concentration.

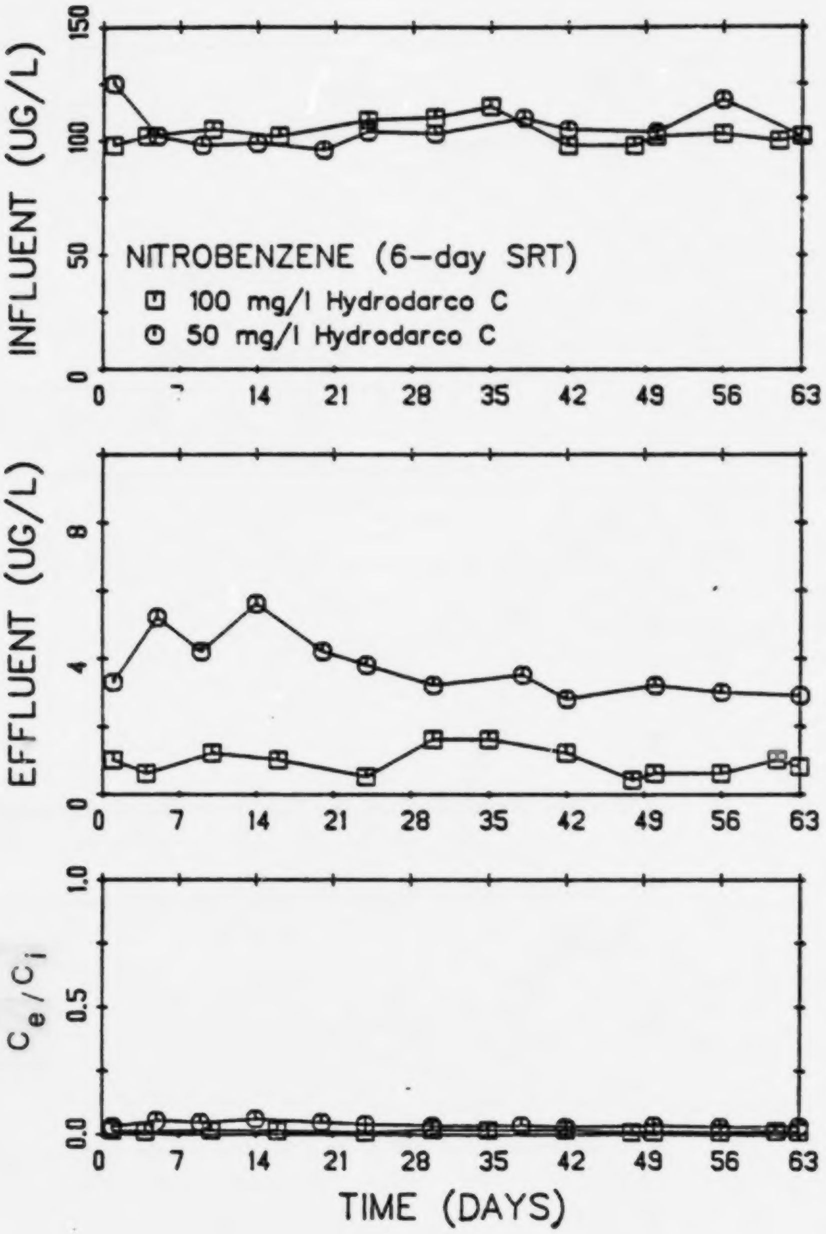


FIGURE 11-43. Comparison of effluent nitrobenzene concentrations from PAC-bioreactor studies with influent PAC doses of 50 and 100 mg/l.

Results from a five week 50 mg/ℓ SA-15 bioreactor study were not significantly different than those obtained for 50 mg/ℓ Hydrodarco C. Nitrobenzene removals in both studies averaged approximately 96%. Effluent concentrations from the 50 mg/ℓ PX-21 bioreactor were approximately equal to the concentrations measured in the effluent from the 100 mg/ℓ Hydrodarco C bioreactor. Nitrobenzene removal in those two studies averaged 98%.

Summaries of the SA-15 and PX-21 bioreactor studies have been given in Table 11-10.

TABLE 11-10

EFFECT OF PAC ADDITION TO ACTIVATED SLUDGE ON REMOVAL OF NITROBENZENE

PAC Dose(mg/ℓ)	Influent (μg/ℓ)	Effluent (μg/ℓ)	Removal (%)
Control	121	4.1	97
	HYDRODARCO C		
50	112	3.7	97
100	108	1.5	99
	SA-15		
50	102	4.6	96
	PX-21		
50	98	2.0	98

11.5.2 Volatile Compounds

Integrated activated sludge/carbon adsorption bioreactor studies were conducted with the volatile biodegradable compounds benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene. All of the studies presented in this section were conducted in bioreactors operated with 6-day solids retention time. Influent PAC doses ranged from 25 to 200 mg/ℓ, and the medium activity PAC Hydrodarco C was used in all of the studies with the volatile, biodegradable compounds. Aeration rates ranged from 3.6 to 4.4 ℓ/min, and the hydraulic retention time was set at 5.5 hours.

11.5.2.1 Benzene

The effect of adding powdered activated carbon to activated sludge bioreactors on the overall removal of benzene was evaluated at influent PAC doses of 25, 50, 100, and 200 mg/ℓ. Results from bioreactor studies conducted with influent PAC doses of 25, 50, and 100 mg/ℓ have been plotted with results from the control activated sludge unit in Figures 11-44, 11-45, and 11-46, respectively. Each figure includes influent, effluent, and off-gas concentrations and N/N_0 values representing the fraction of the influent fluxes measured in effluents and off-gases combined.

No significant improvement in overall benzene removal occurred in reactors receiving PAC doses of 25, 50 and 100 mg/ℓ compared to the control unit, as shown by the comparisons in Figures 11-44 through 11-46. Overall benzene removals in control and 25, 50, and 100 mg/ℓ PAC units were approximately the same, averaging 83%, 79%, 84%, and 86%, respectively. Even the addition of 100 mg/ℓ had little effect upon effluent and off-gas concentrations which averaged approximately 0.6 μg/ℓ and less than 150-ng/ℓ, respectively, in both control and 100 mg/ℓ PAC bioreactors. The influent PAC concentration to the bioreactor receiving 25 mg/ℓ powdered activated carbon was increased to 200 mg/ℓ on Day 74. As the results in Figure 11-47 illustrate, the eight-fold increase in influent PAC concentration did not significantly improve the overall removal of benzene. Overall benzene removals measured in the 25, 50, and 100 mg/ℓ PAC bioreactors have been graphically compared with the overall removals observed in the control activated sludge unit in Figure 11-48. Table 11-11 gives the average values for influent, effluent, and off-gas concentrations and overall removals observed for the various PAC bioreactor studies.

A 10-liter bioreactor without activated sludge was operated in a continuous flow mode with an influent composed of synthetic wastewater spiked with benzene and slurried PAC, to determine the maximum benzene removal attributable solely to adsorption. Two influent PAC concentrations were considered, 50 and 100 mg/ℓ. Results from these two studies have been compared with results obtained from the 50 and 100 mg/ℓ PAC sludge bioreactor studies in Figure 11-49 and Table 11-12. Overall benzene removal due solely to adsorption in the PAC units without activated sludge biomasses averaged only 19% and 26% for influent PAC doses of 50 and 100 mg/ℓ, respectively. Overall removals in activated sludge units receiving 50 and 100 mg/ℓ of PAC were significantly larger, averaging 84 and 86%, respectively. Biodegradation of benzene in the control activated sludge unit averaged 83%. This set of results suggests that the dominant removal mechanism in the activated sludge units receiving slurried PAC was biodegradation by the activated sludge microorganisms rather than PAC adsorption.

11.5.2.2. Ethylbenzene

Powdered activated carbon/activated sludge studies with ethylbenzene were conducted with influent PAC concentrations ranging

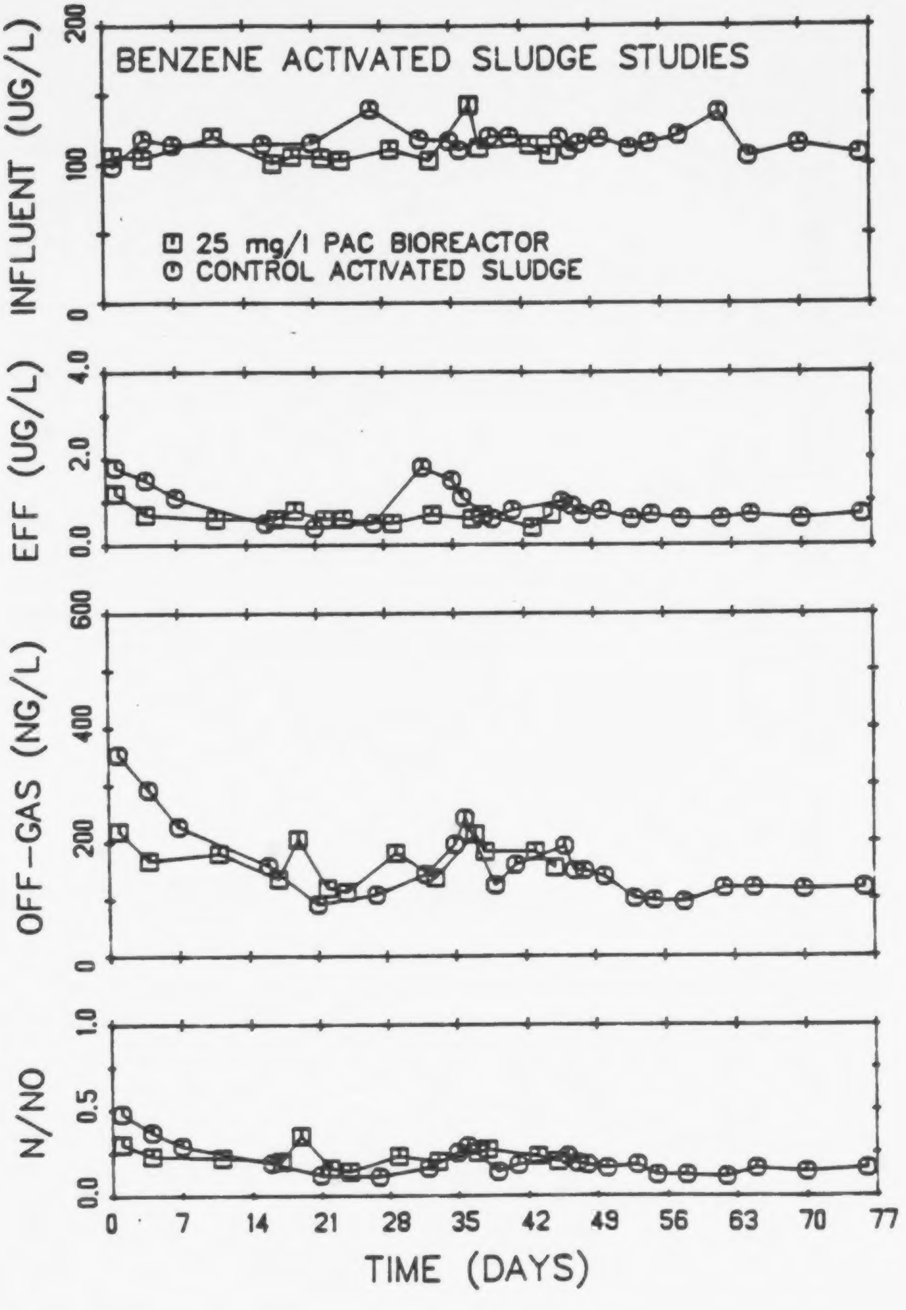


FIGURE 11-44. Effect of a 25 mg/l influent PAC dose on benzene effluent and off-gas concentrations and fractional recoveries, N/No.

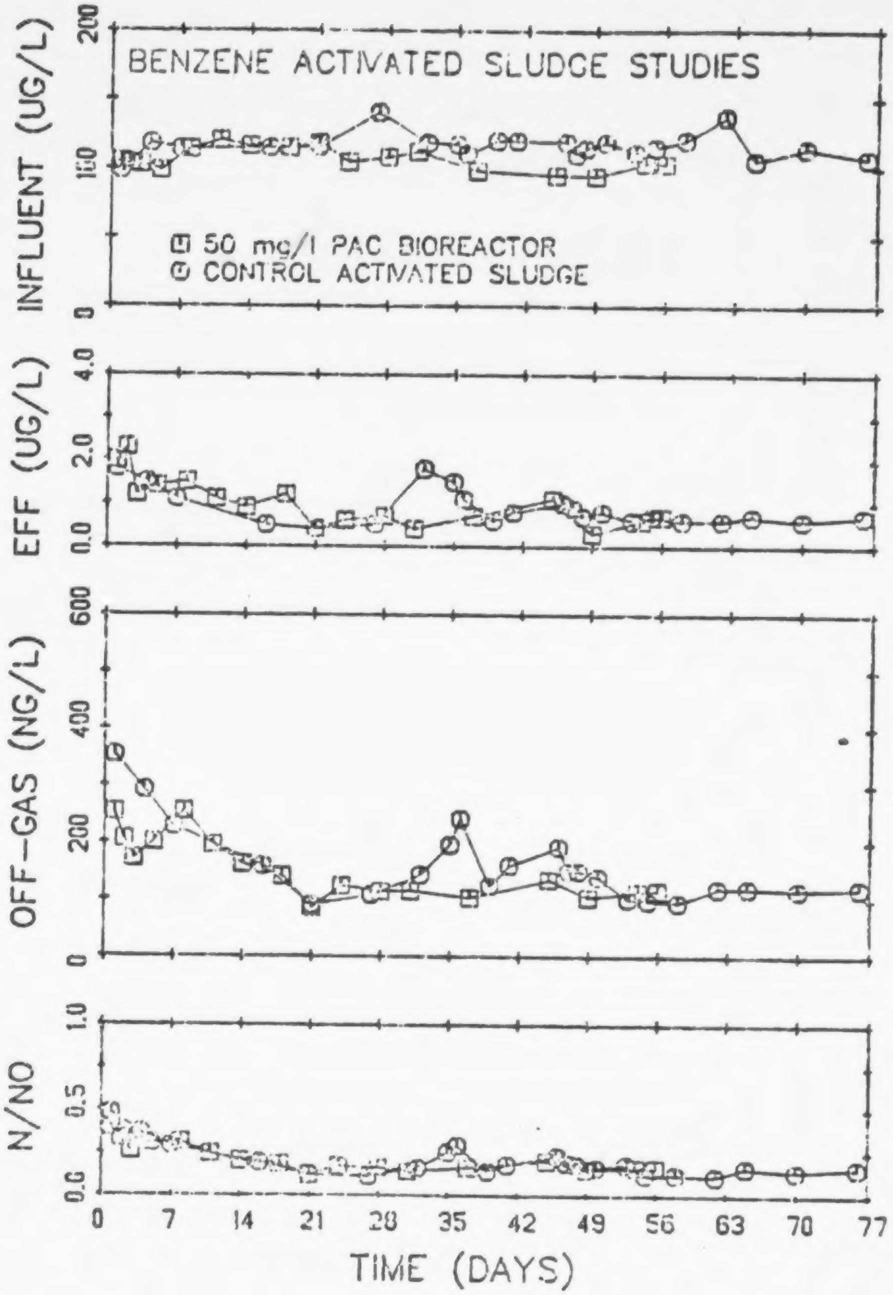


FIGURE 11-45. Effect of a 50 mg/l influent PAC dose on benzene effluent and off-gas concentrations and fractional recoveries, N/No.

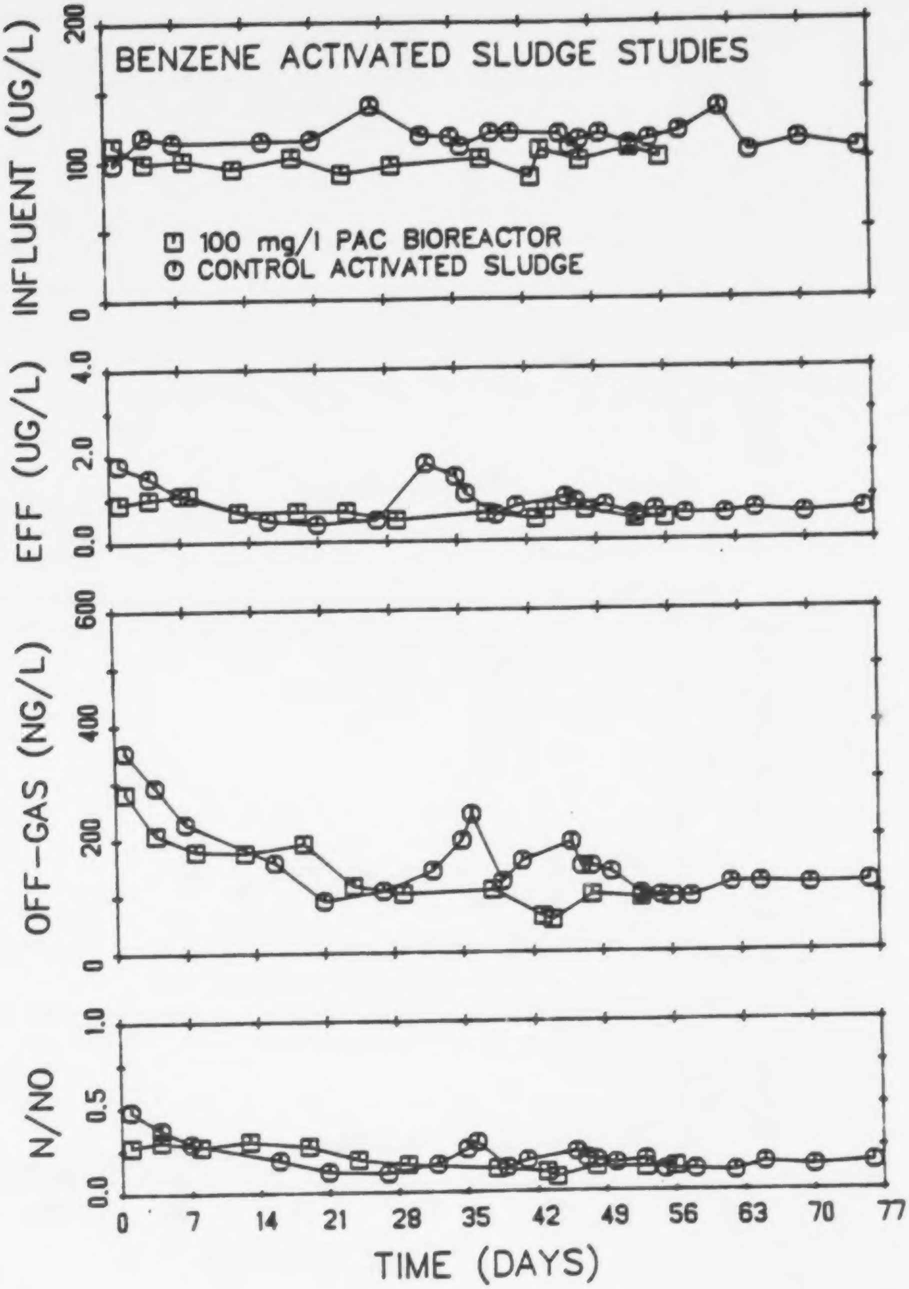


FIGURE 11-46. Effect of a 100 mg/l influent PAC dose on benzene effluent and off-gas concentrations and fractional recoveries, N/No.

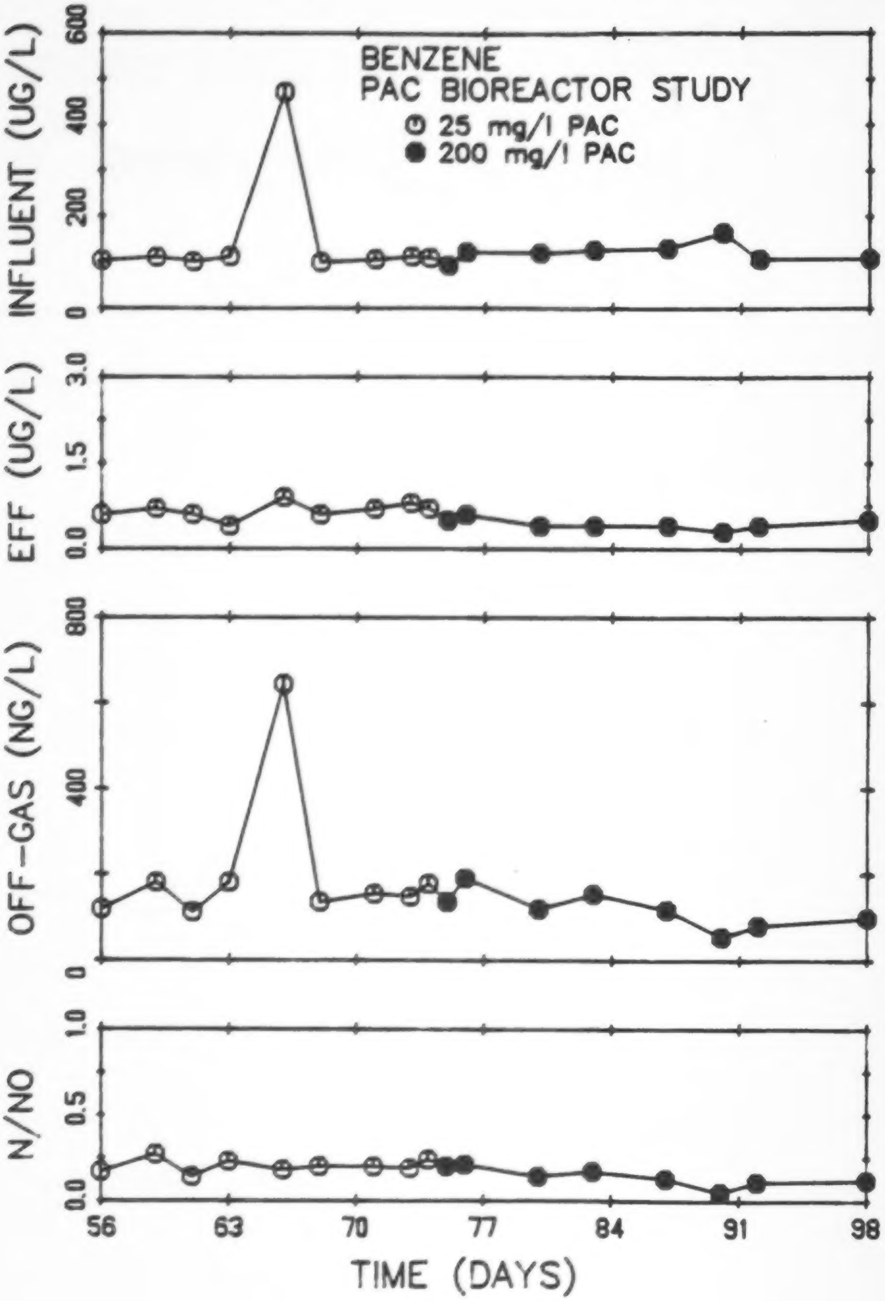


FIGURE 11-47. Effect of increasing the influent PAC dose from 25 to 200 mg/l on the benzene effluent and off-gas concentration and fractional recovery, N/No.

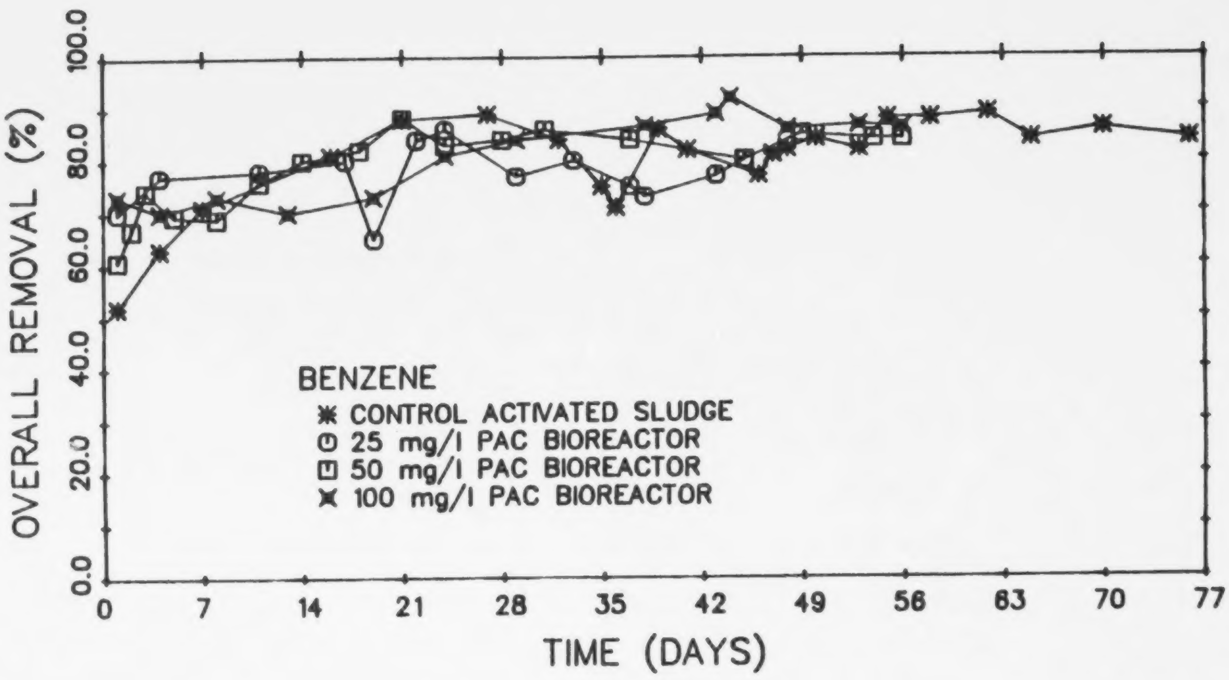


FIGURE 11-48. Comparison of benzene overall removals due to biodegradation and PAC adsorption measured during a control activated sludge study and PAC-bioreactor studies with influent PAC doses of 25, 50, and 100 mg/l of Hydrodarco C.

TABLE 11-11

EFFECT OF INFLUENT PAC DOSE ON STEADY-STATE BENZENE REMOVAL IN 10-LITER BIOREACTORS OPERATED WITH 6-DAY SRT's

Influent PAC Dose (mg/ℓ)	Influent (μg/ℓ)	Effluent (μg/ℓ)	Off-Gas (ng/ℓ)	Overall Removal[+] (%)
Control	118 (8.4)	0.8(0.4)	142(40)	83.1 (5.2)
25	110 (11.1)	0.6(0.1)	112 (13)	79.0 (4.4)
50	106 (8.3)	0.7(0.3)	119(21)	83.7 (2.4)
100	100 (7.4)	0.6(0.1)	92(22)	86.4 (3.2)
200	123 (21.4)	0.4(0.1)	119(42)	85.9 (5.2)

[+] Overall Removal = $(1-N/N_o)x100$

( ) Standard Deviation

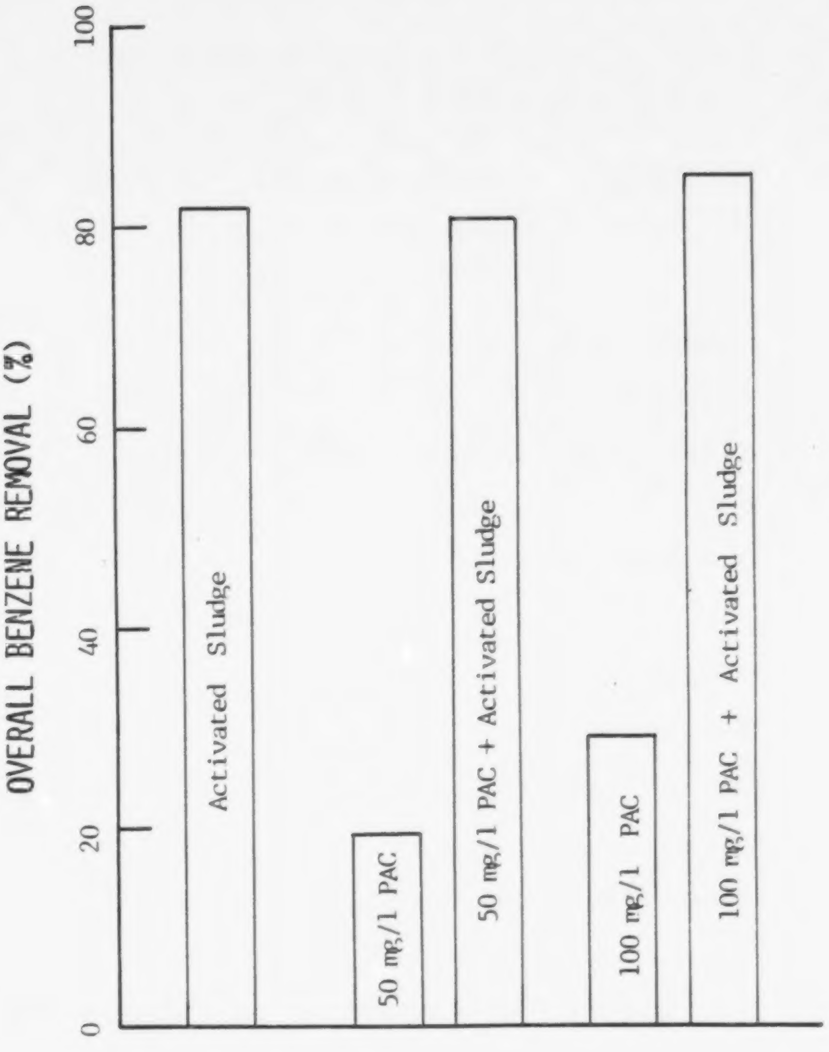


FIGURE 11-49. Overall benzene removals measured in continuous flow 10-liter bioreactor studies with activated sludge, Hydrodarco C PAC without activated sludge, and activated sludge with PAC.

TABLE 11-12

BENZENE REMOVALS MEASURED IN CONTINUOUS FLOW 10-LITER BIOREACTOR STUDIES WITH ACTIVATED SLUDGE, PAC WITHOUT ACTIVATED SLUDGE, AND ACTIVATED SLUDGE WITH PAC

OPERATING CONDITIONS

Parameter	SW[1]	SW & A/S[2]	SW & PAC[3]	SW, A/S & PAC[4]
		50 mg/ℓ PAC		
Influent (μg/ℓ)	94	118	105	106
Effluent (μg/ℓ)	3.4	0.8	2.4	0.7
Off-Gas (ng/ℓ)	652	142	660	119
N/N_o	0.96	0.17	0.81	0.16
Overall Removal (%)	4	83	19	84
		100 mg/ℓ PAC		
Influent (μg/ℓ)			111	100
Effluent (μg/ℓ)			3.2	0.6
Off-Gas (ng/ℓ)			593	92
N/N_o			0.74	0.14
Overall Removal (%)			26	86

1. Baseline studies without activated sludge or PAC in the bioreactor
2. Control activated sludge bioreactor (no PAC-addition)
3. Bioreactor without activated sludge receiving slurried PAC
4. Bioreactor with activated sludge receiving slurried PAC

from 25 to 200 mg/ℓ in bioreactors operated at 6-day SRT's. The PAC used in the ethylbenzene studies was Hydrodarco C. Results from bioreactors receiving 25, 50 and 100 mg/ℓ PAC have been compared with results from control activated sludge studies in Figures 11-50, 11-51, and 11-52, respectively. Each figure includes measured influent, effluent, and off-gas concentrations and N/N_0 values representing the fraction of the influent fluxes measured in effluents and off-gases combined.

There was no difference in ethylbenzene removal in control and 25 mg/ℓ bioreactors as indicated by the similarities of the N/N_0 curves in Figure 11-50. Both reactors experienced an approximate 14-day acclimation period preceding steady-state ethylbenzene removal. The comparison of N/N_0 values measured during the acclimation phase and under steady-state conditions given in Table 11-13 shows that comparable increases in overall removals occurred in both the control activated sludge and 25 mg/ℓ PAC bioreactors.

The results for the 50 mg/ℓ PAC bioreactor presented in Figure 11-51 have been compared to a parallel control reactor. As noted in the discussion of results from activated bioreactor studies in Section 10, bioreactor performance with respect to toxics removal during the acclimation period from replicate studies have varied slightly, but steady-state removals typically yielded comparable results. Ethylbenzene addition to the 50 mg/ℓ PAC bioreactor was begun on Day zero while slurried PAC addition was initiated on Day 7. Prior to PAC addition ethylbenzene removal in the two reactors was nearly identical, as evidenced by the similarities in the N/N_0 curves. The overall removal of ethylbenzene increased from approximately 30 to 60% within 24 hours after the 50 mg/ℓ PAC addition was begun, while the removal in the control unit remained at 30%. Both control activated sludge and 50 mg/ℓ PAC bioreactors exhibited a significant increase in the overall ethylbenzene removal on Day 14, and steady-state removal was achieved by Day 21. Results from the 50 mg/ℓ PAC unit demonstrated that PAC addition during the acclimation phase effected decreases in effluent and off-gas concentrations, and hence an increase in overall ethylbenzene removal. An interesting feature of the results from the 50 mg/ℓ PAC bioreactor was the continued acclimation of the activated sludge microorganisms to ethylbenzene after PAC addition was begun. The greatest benefit to accrue from the 50 mg/ℓ PAC dose occurred between Days 7 and 18, before the activated sludge bioreactor units became fully acclimated. After Day 18 the overall ethylbenzene removal was only slightly larger in the PAC unit, averaging 84% compared to 80% in the control activated sludge bioreactor.

The addition of a 100 mg/ℓ influent PAC dose produced a significant improvement in ethylbenzene removal during the initial two to three week phase, as shown in Figure 11-52. Additions of both ethylbenzene and slurried PAC to the activated sludge and 100 mg/ℓ PAC bioreactor influents were begun on Day 0. After the first 14 days differences in effluent and off-gas concentrations and overall removals were considerably reduced, but the average overall ethylbenzene removal remained slightly larger in the PAC unit throughout the length of the

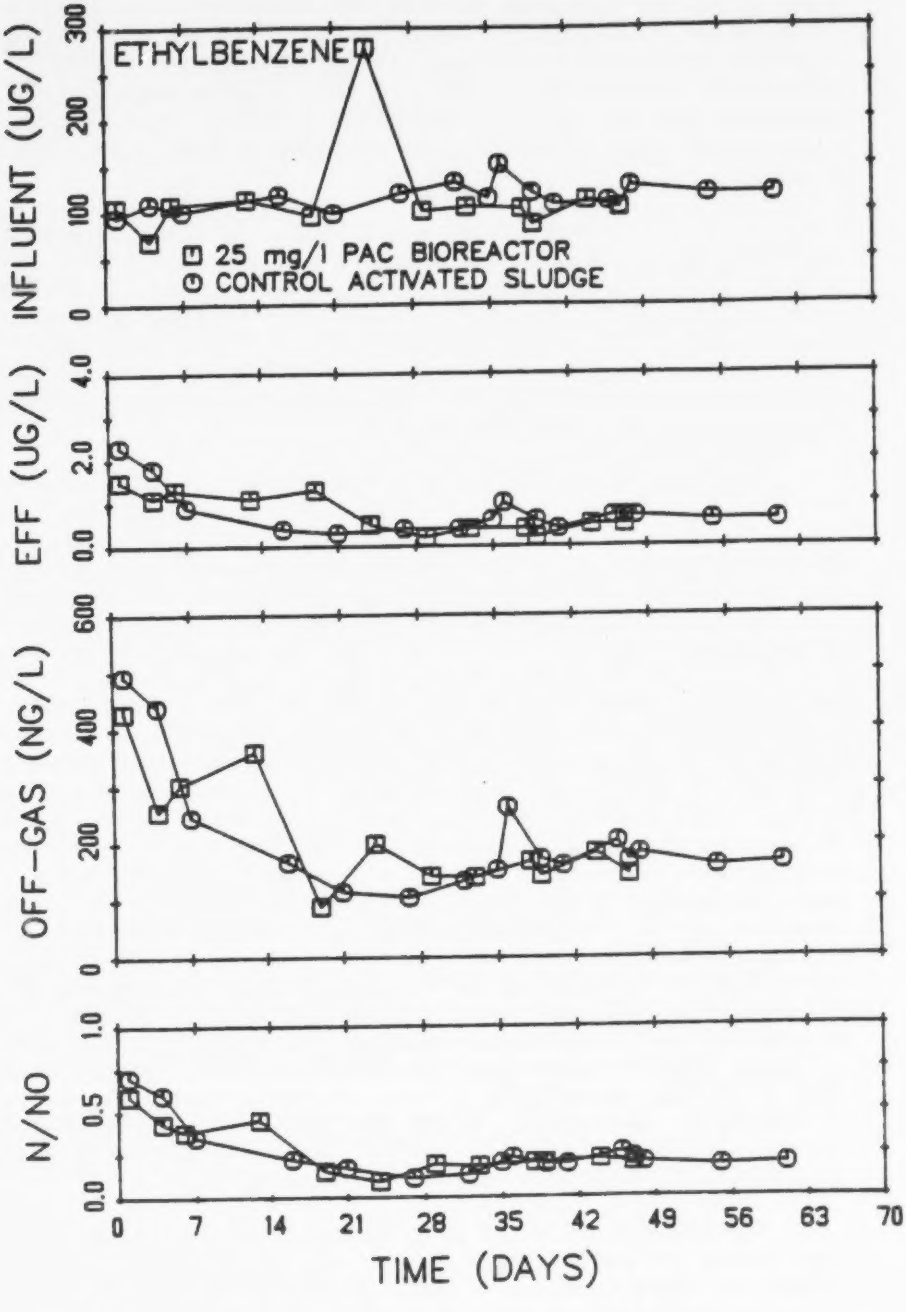


FIGURE 11-50. Effect of a 25 mg/l influent PAC dose on ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No.

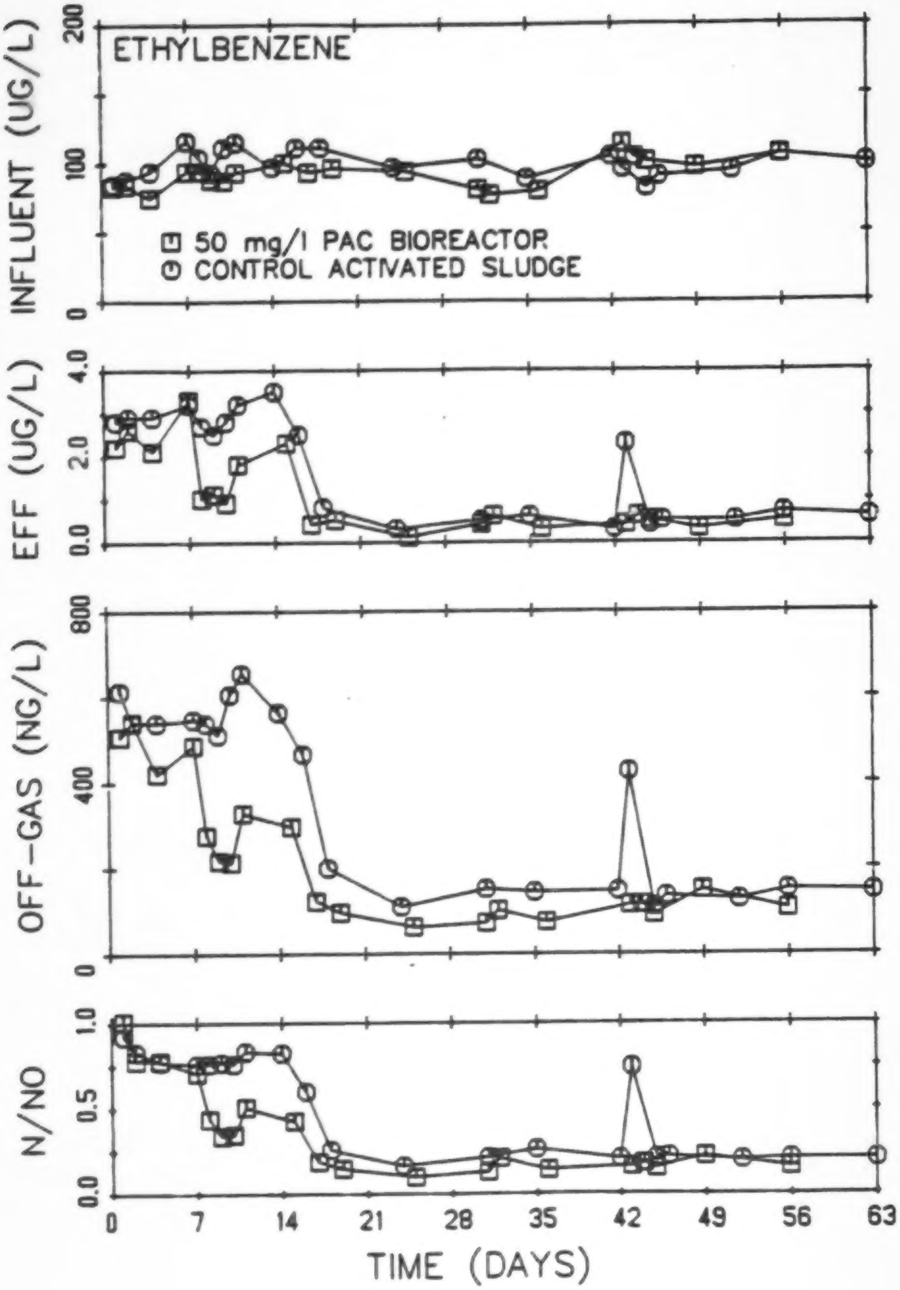


FIGURE 11-51. Effect of a 50 mg/l influent PAC dose on ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No.

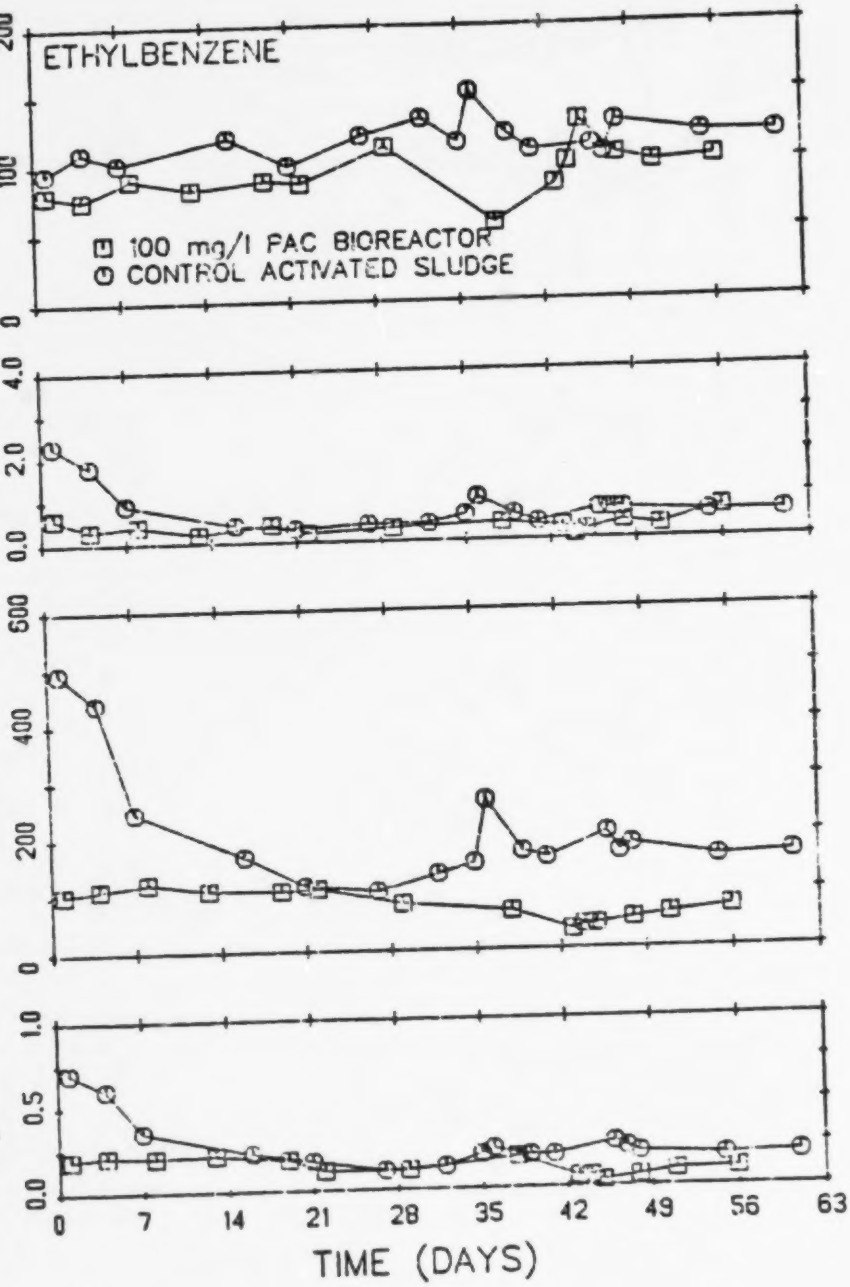


FIGURE 11-52. Effect of a 100 mg/l influent PAC dose on ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No.

TABLE 11-13

COMPARISON OF ETHYLBENZENE N/N_0 VALUES FROM ACCLIMATION PERIODS AND STEADY-STATE CONDITIONS IN CONTROL AND 25 mg/ℓ PAC BIOREACTORS

	Acclimation Period		
Bioreactor	Day 1	Day 4	Steady-state (average)
Control	0.72	0.43	0.19
25 mg/ℓ	0.61	0.42	0.19

TABLE 11-15

COMPARISON OF N/N_0 DATA FROM CONTROL AND PAC BIOREACTORS FOR CHLOROBENZENE

Bioreactor	Day 1	Day 3	Steady-state (average)
Control	0.53	0.45	0.19
25 mg/ℓ	0.29	0.25	0.19
50 mg/ℓ	0.21	0.22	0.17
100 mg/ℓ	0.18	0.15	0.10

study. Results from the 100 mg/ℓ PAC reactor showed no acclimation period as was observed for the other ethylbenzene studies. The PAC added to the influent had sufficient adsorption capacity to prevent significant discharges of ethylbenzene in the effluent and off-gas during the early stages of the acclimation period when the amount biodegraded in the control unit was small.

Results from control and 25, 50 and 100 μg/ℓ PAC bioreactors have been compared in Figure 11-53. Influent, effluent and off-gas concentrations averaged during periods of steady-state ethylbenzene removal are summarized by Table 11-14.

The effect of an eight-fold increase in influent PAC concentration on ethylbenzene removal was studied by increasing the PAC dose from 25 to 200 mg/ℓ. On Day 75 of the 25 mg/ℓ PAC bioreactor study, the influent Hydrodarco C dose was increased to 200 mg/ℓ by adjusting the concentration of the PAC slurry. The change in PAC dose effected only a slight increase in overall ethylbenzene removal, as evidenced by the N/N_0 curve in Figure 11-54. Overall ethylbenzene removal averaged 78% during the 25 mg/ℓ PAC dosing period compared to 87% during the 200 mg/ℓ PAC dosing period.

11.5.2.3. Chlorobenzene

Powdered activated carbon/activated sludge studies were conducted with chlorobenzene at influent PAC doses ranging from 25 to 200 mg/ℓ in bioreactors operated at 6-day SRT's. The PAC used in these studies was Hydrodarco C. Influent, effluent and off-gas concentrations measured in PAC bioreactor studies with 25, 50, and 100 mg/ℓ PAC have been plotted in Figures 11-55, 11-56, and 11-57, respectively, with values from the control activated sludge unit. Also included in each figure are N/N_0 values representing the fraction of the influent fluxes measured in effluents and off-gases combined. Chlorobenzene and slurried PAC additions to the influents were initiated on Day zero.

Results from the PAC bioreactor studies showed that the addition of PAC produced the most significant improvements in overall chlorobenzene removals, compared to control reactors, during the first 7 to 14 days after the initial additions of PAC and chlorobenzene to the influents. This time period corresponded to the microbial acclimation phase observed for all of the biodegradable compounds in control activated sludge studies. The comparison of data from control and PAC reactors on Days 1 and 3 given in Table 11-15 shows that enhanced removal was most significant at the beginning of the studies. After the acclimation period the results from the control activated sludge and PAC bioreactors receiving 25 and 50 mg/ℓ influent PAC were nearly identical. Steady-state overall removals averaged 81%, 81%, and 83% in control activated sludge and 25 and 50 mg/ℓ PAC bioreactors, respectively.

The overall removal of chlorobenzene in the 100 mg/ℓ PAC unit was consistently better than that observed in the control reactor as shown by Figure 11-57. The improvement in chlorobenzene removal was most significant during the acclimation period. Under steady-state conditions the differences in effluent and off-gas concentrations

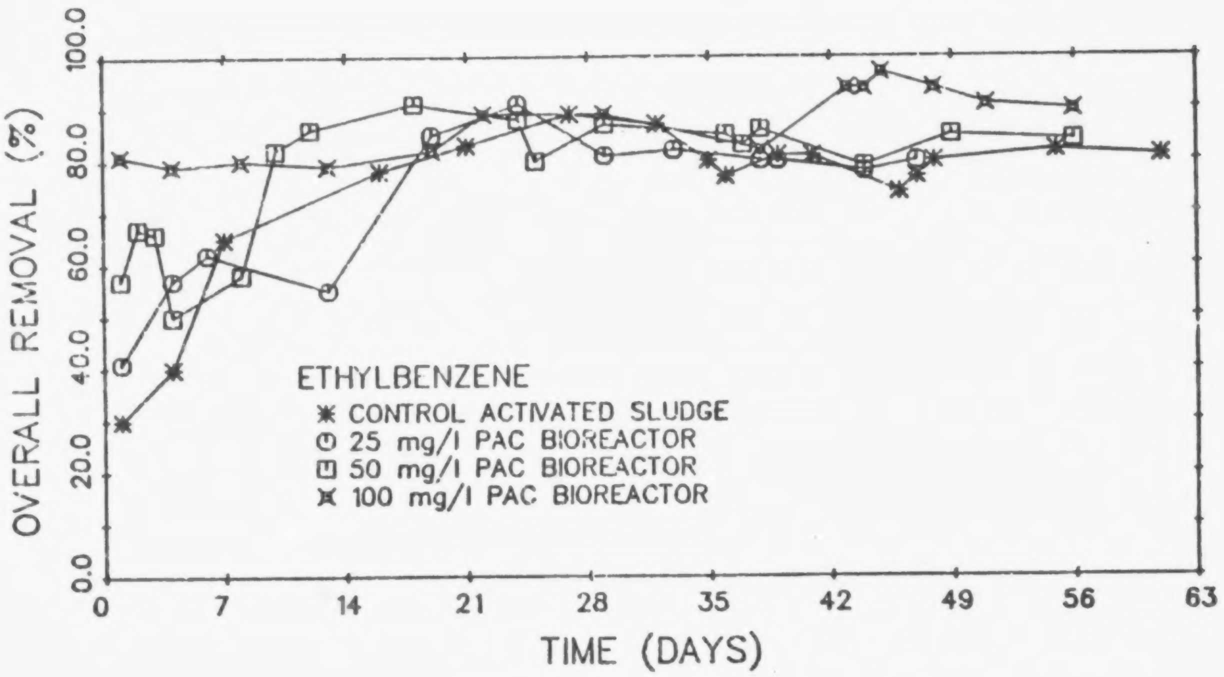


FIGURE 11-5 3. Comparison of ethylbenzene removals due to biodegradation and PAC adsorption measured during a control activated sludge study and PAC-bioreactor studies with influent PAC doses of 25, 50, and 100 mg/l of Hydrodarco C.

TABLE 11-14

EFFECT OF INFLUENT PAC DOSE ON STEADY-STATE ETHYLBENZENE REMOVAL IN 10-LITER BIOREACTORS WITH 6-DAY SRT'S

Influent PAC Dose (mg/l)	Influent (ug/l)	Effluent (ug/l)	Off-Gas (ng/l)	Overall Removal[+] (%)
Control	119 (14.4)	0.6 (0.2)	166 (43)	81 (4.0)
25	109 (6.2)	0.6 (0.1)	165 (13)	78.5 (2.0)
50	94 (11.2)	0.4 (0.1)	98 (25)	84.7 (3.5)
100	92 (17.9)	0.3 (0.1)	79 (31)	87.2 (6.5)
200	118 (20.5)	0.2 (0.1)	98 (23)	87.4 (2.8)

[+] Overall Removal = $(1-N/N_o) \times 100$

( ) Standard deviation

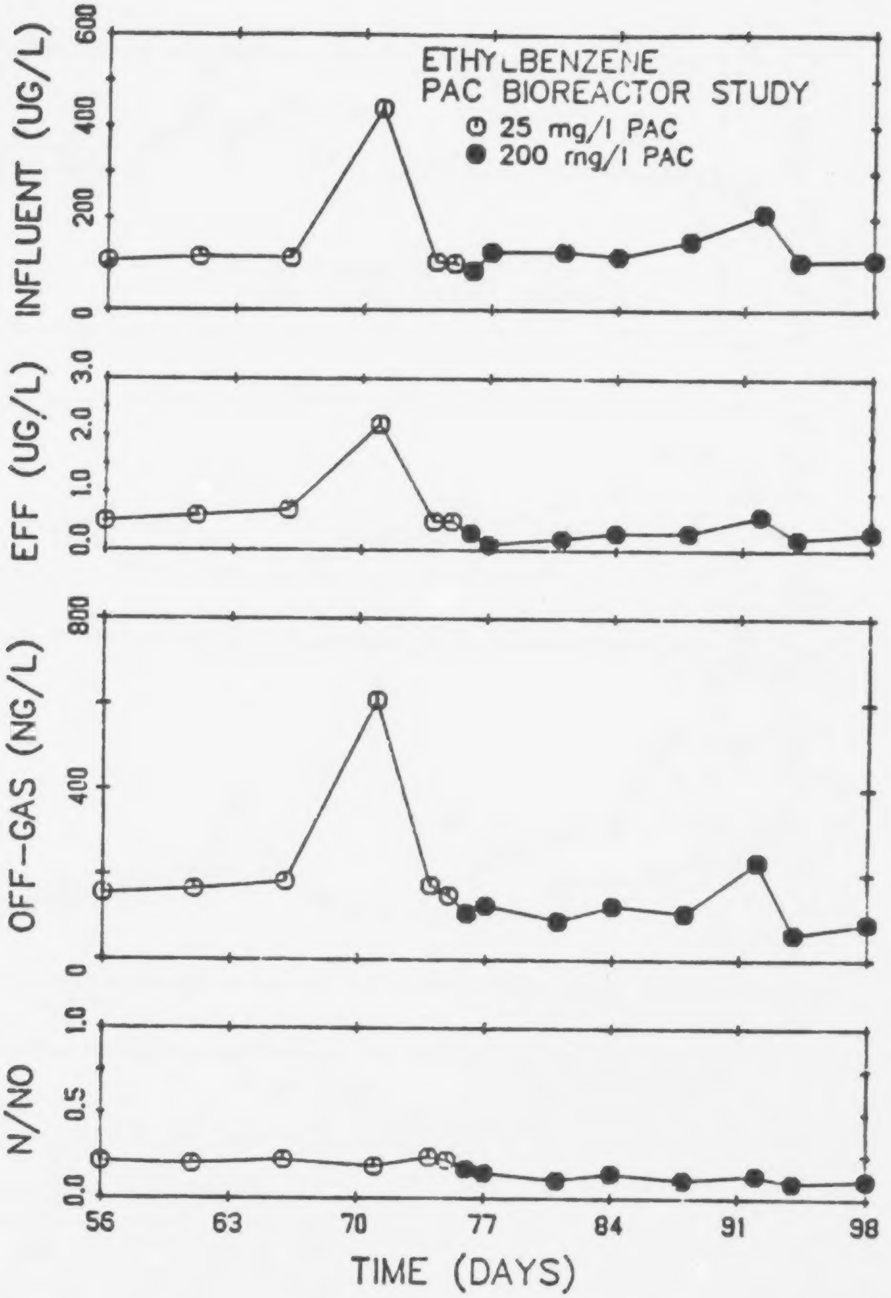


FIGURE 11-54. Effect of increasing the influent PAC dose from 25 to 200 mg/l on the ethylbenzene effluent and off-gas concentration and fractional recovery, N/No.

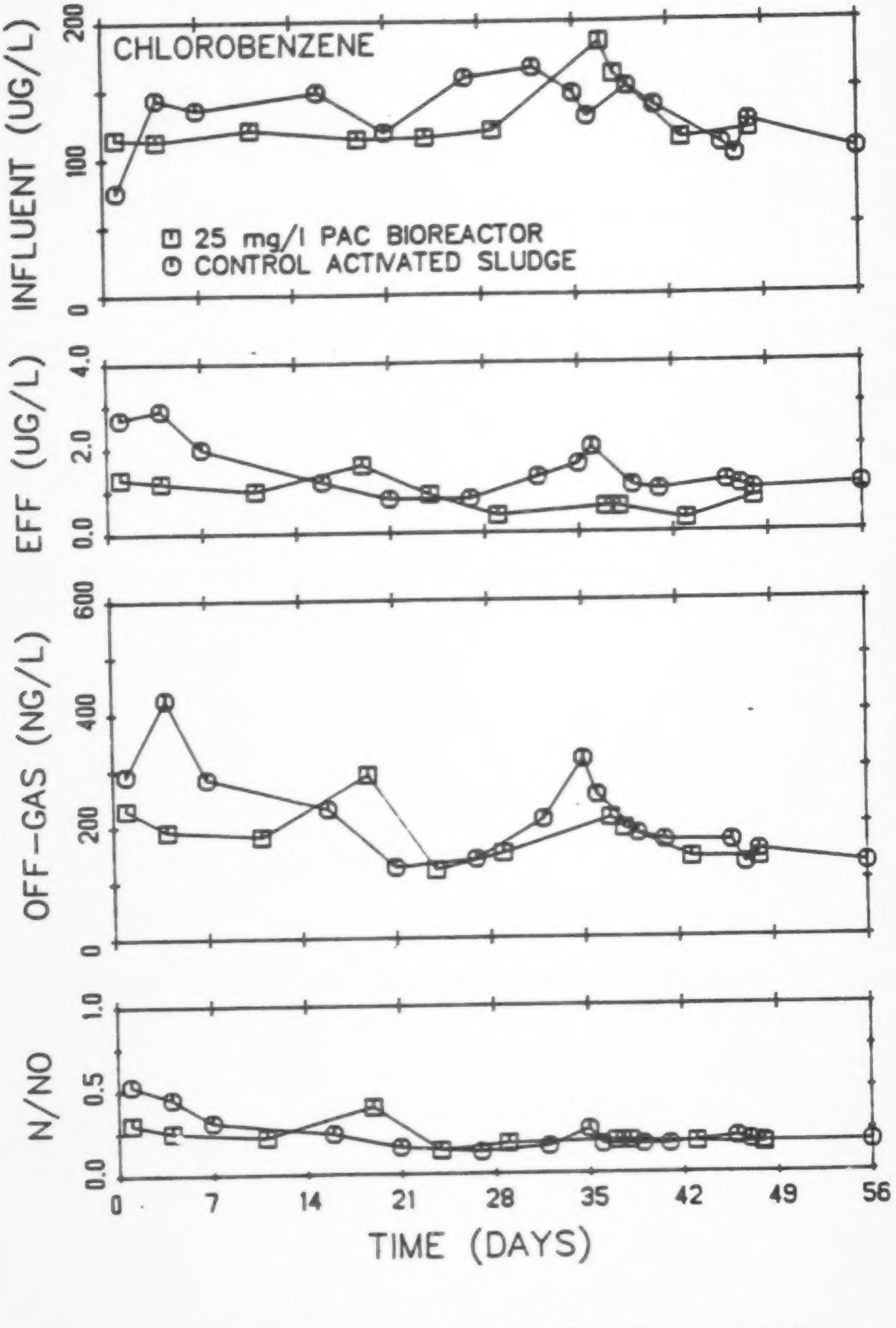


FIGURE 11-55. Effect of a 25 mg/l influent PAC dose on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

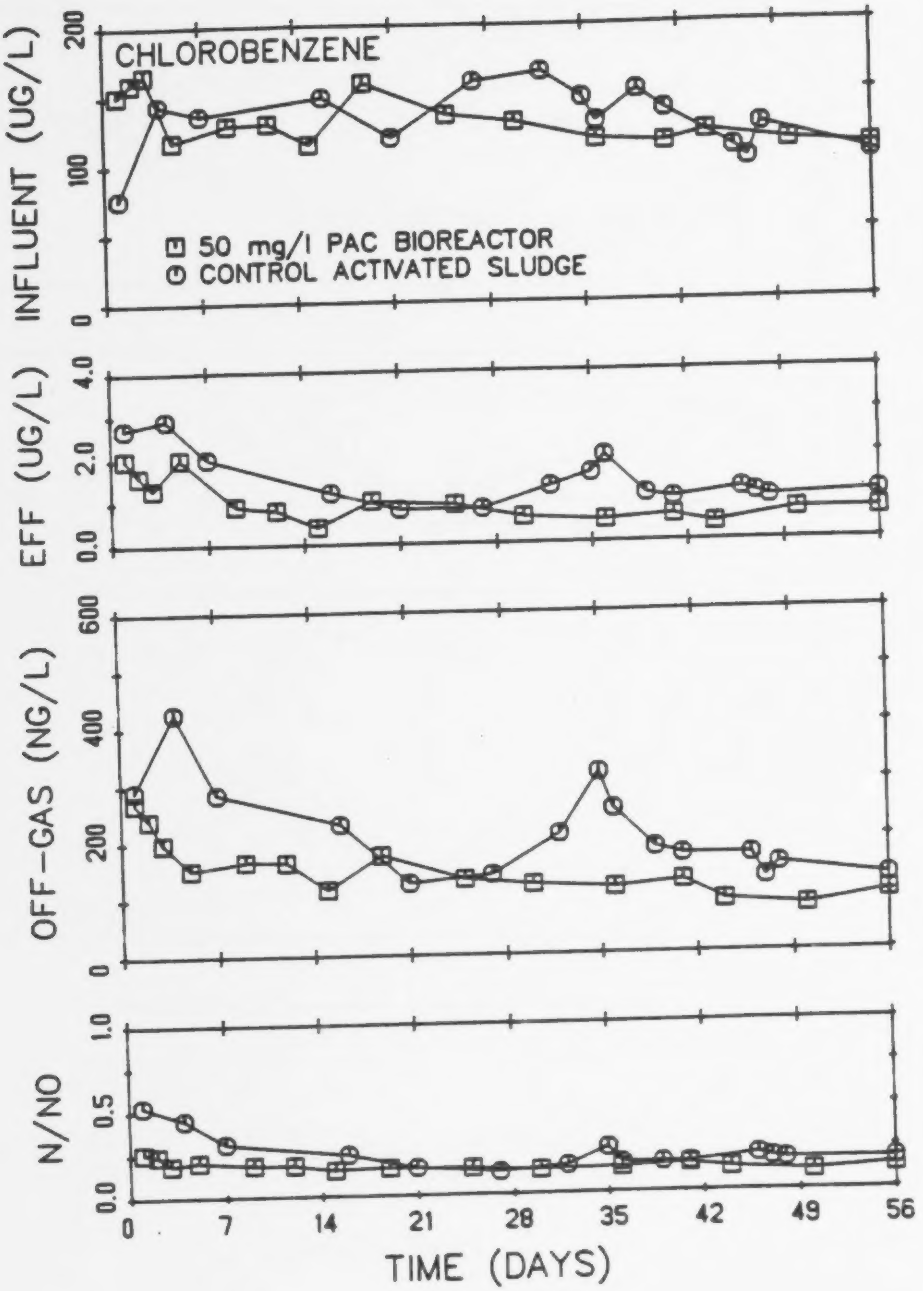


FIGURE 11-56. Effect of a 50 mg/l influent PAC dose on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

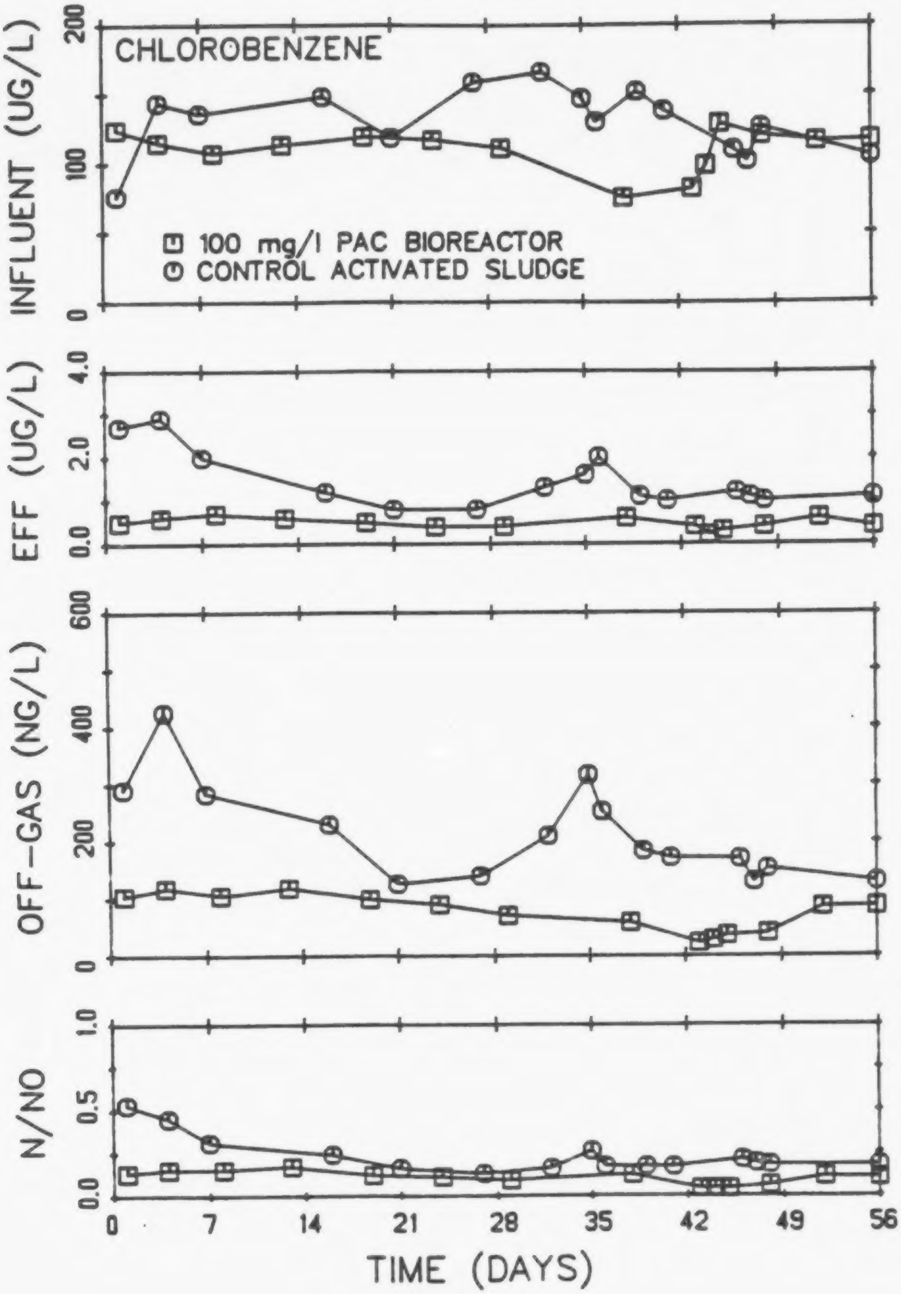


FIGURE 11-57. Effect of a 100 mg/l influent PAC dose on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

between the control and 100 mg/ℓ PAC reactors were considerably reduced. The results recorded during the 100 mg/ℓ PAC study show the absence of an acclimation period during the initial two weeks of operation. Effluent and off-gas concentrations observed on Day 1 were approximately the same as those measured throughout the study.

A comparison of overall chlorobenzene removal from control and 25, 50 and 100 mg/ℓ PAC bioreactors has been provided in Figure 11-58. Summaries of influent, effluent and off-gas concentrations and overall removals averaged from steady-state toxics removal periods are given by Table 11-16.

The effect of an eight-fold change in influent PAC concentration on chlorobenzene removal was examined by increasing the PAC dose from 25 to 200 mg/ℓ. On Day 74 of the 25 mg/ℓ PAC study previously described, the influent concentration of Hydrodarco C was increased to 200 mg/ℓ by adjusting the concentration of the PAC slurry. As the results in Figure 11-59 indicate, there was only a slight decrease in the fractional recovery, N/N_0, of chlorobenzene. Overall chlorobenzene removal averaged 82% during the 25 mg/ℓ PAC period compared to 90% during the 200 mg/ℓ influent PAC dose. The results for chlorobenzene during the two influent PAC concentrations have been summarized in Table 11-16. Benzene, ethylbenzene, and chlorobenzene, all three biodegradable compounds, exhibited only slight changes in overall removals attributable to the 8-fold increase in influent PAC dose. In general, the greater the amount of a compound removed by biodegradation, the less was the effect of increasing the influent PAC dose.

11.5.2.4. Toluene

A single-solute PAC-bioreactor study with toluene was conducted at an influent Hydrodarco C concentration of 200 mg/ℓ. Results from this study are compared to results from a parallel operated control activated reactor in Figure 11-60. Toluene and slurried PAC were initially added to the influents on Day 0.

The results in Figure 11-60 show that the greatest improvement in toluene removal occurred during the 14 to 21 day acclimation phase. After Day 21 differences in fractional recovery values measured in the control and PAC bioreactor decreased. As shown by the comparison of average overall removals in Table 11-17, the reactor receiving 200 mg/ℓ PAC yielded lower effluent and off-gas concentrations, and hence better overall toluene removal. A significant finding was that the magnitude of the differences between control and PAC reactors was relatively small for such a large influent PAC dose. The results were consistent with the observation that the benefit of PAC-addition for enhanced toxics removal decreased as biodegradation increased.

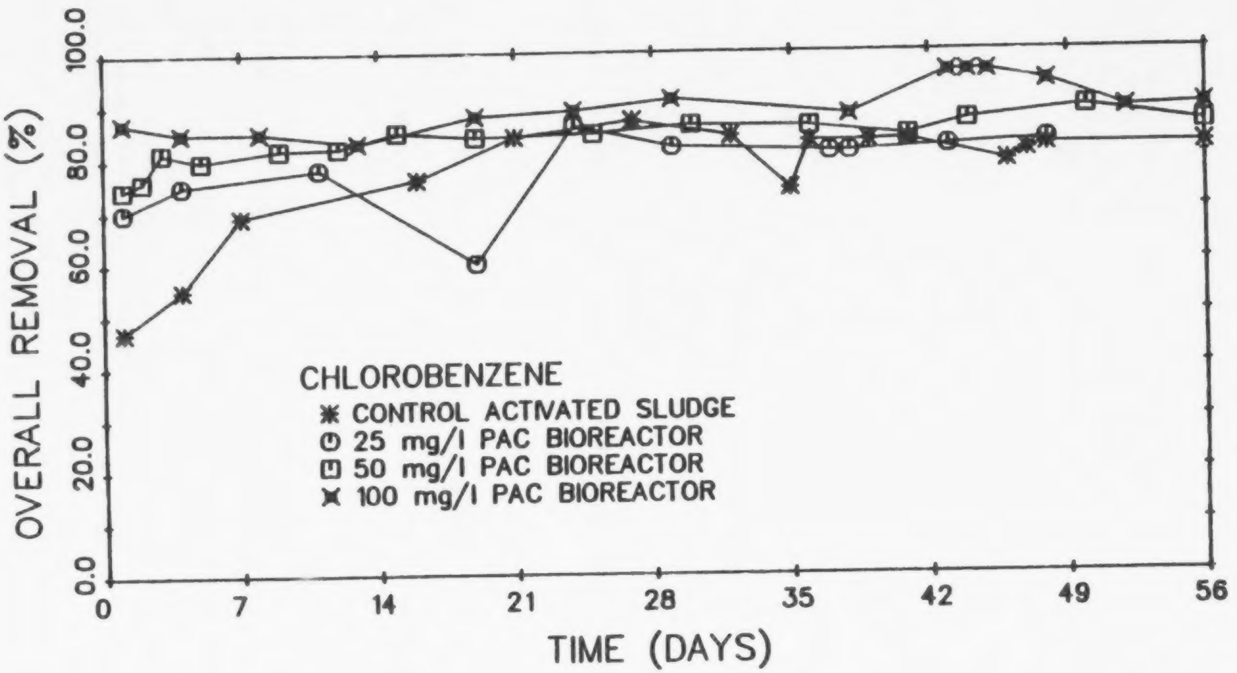


FIGURE 11-58. Comparison of chlorobenzene overall removals due to biodegradation and PAC adsorption measured during a control activated sludge study and PAC-bioreactor studies with influent PAC doses of 25, 50, and 100 mg/l of Hydrodarco C.

TABLE 11-16

EFFECT OF INFLUENT PAC DOSE ON STEADY-STATE CHLOROBENZENE REMOVAL IN 10-LITER BIOREACTORS WITH 6-DAY SRT'S

Influent PAC Dose (mg/l)	Influent (ug/l)	Effluent (ug/l)	Off-Gas (ng/l)	Overall Removal[+] (%)
Control	133 (21.6)	1.1 (0.3)	192 (57)	82.1 (2.5)
25	111 (9.1)	0.5 (0.2)	142 (22)	81.7 (1.5)
50	127 (17.2)	0.8 (0.4)	134 (35)	84.3 (2.6)
100	110 (15.3)	0.5 (0.1)	76 (33)	89.7 (4.3)
200	109 (9.8)	0.3 (0.1)	76 (15)	90.0 (2.1)

[+] Overall Removal = $(1-N/N_o) \times 100$

( ) Standard deviation

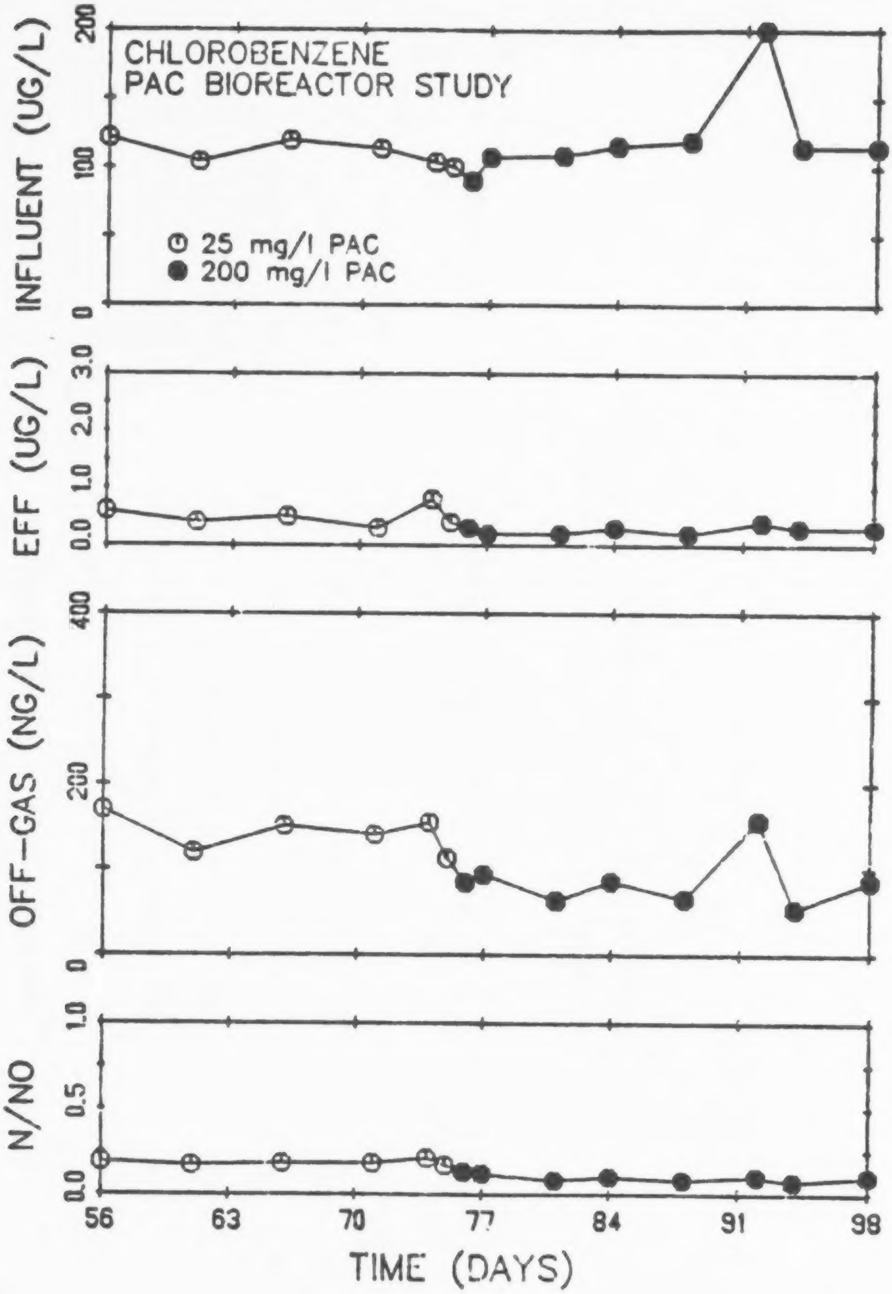


FIGURE 11-59. Effect of increasing the influent PAC dose from 25 to 200 mg/l on the effluent and off-gas chlorobenzene concentrations and fractional recovery, N/No.

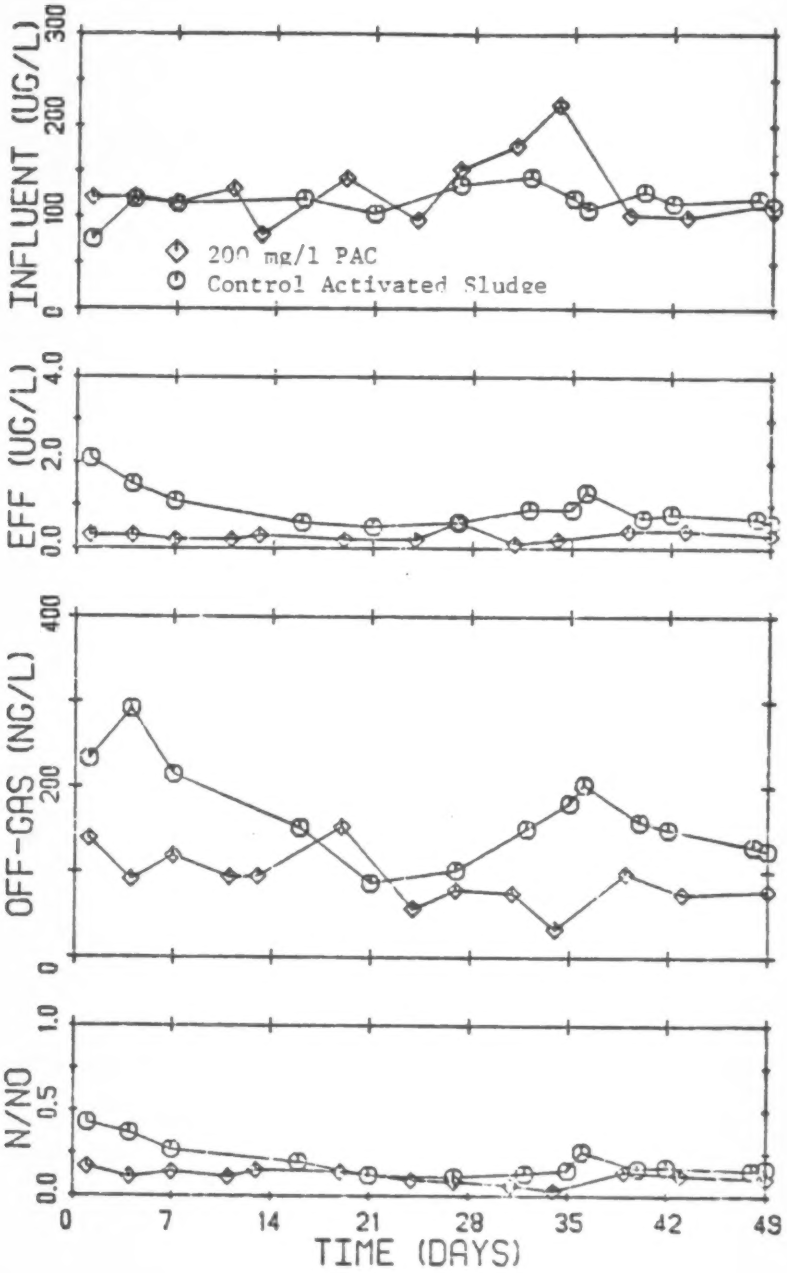


FIGURE 11-60. Effect of a 200 mg/l influent PAC dose on toluene effluent and off-gas concentrations and fractional recoveries, N/No.

TABLE 11-17

COMPARISON OF TOLUENE REMOVALS IN CONTROL AND 200 mg/ℓ PAC BIOREACTORS

	Control		200 mg/ℓ PAC	
Parameter	Day 1	Average+	Day 1	Average+
Influent (μg/ℓ)	76.0	120 (12)++	122	132 (46)
Effluent (μg/ℓ)	2.1	0.8 (0.2)	0.3	0.3 (0.2)
Off-gas (ng/ℓ)	233	142 (32)	139	82 (33)
N/N_o	0.43	0.16 (0.04)	0.17	0.10 (0.04)
Reduction in Aqueous Conc (%)	97.2	99.4 (0.2)	99.8	99.7 (0.2)
Overall Removal (%)	57	84 (4)	83	90 (4)

+Average values calculated from data collected after Day 14

++Numbers in parentheses are standard deviation values

11.5.2.5. O-Xylene

Single solute PAC bioreactor studies with o-xylene were conducted at only one influent PAC dose, 50 mg/ℓ. The powdered carbon used was Hydrodarco C. Results from this study have been plotted with results from a parallel control activated sludge study in Figure 11-61. Day 0 marked the beginning of o-xylene addition to the two units and PAC addition was started on Day 7. Prior to Day 7 results from both reactors were nearly identical.

Effluent and off-gas concentrations decreased measurably on Day 8 in response to the addition of 50 mg/ℓ slurried Hydrodarco C. The PAC bioreactor gave better overall o-xylene removal between Days 7 and 18. As the results show, the control unit yielded consistent recoveries of approximately 85% during the first fourteen days. The significant decrease in effluent and off-gas concentrations of the control reactor occurred between the second and third weeks of operation indicating the activated sludge microorganisms had acclimated to o-xylene. Once acclimation occurred there was no significant difference in steady-state performances between the 50 mg/ℓ PAC and control activated sludge bioreactor.

An important finding was that the 50 mg/ℓ PAC unit appeared less susceptible to upset conditions which resulted in measurably reduced o-xylene removal in the activated sludge reactor. The control unit experienced two occasions in which o-xylene recoveries suddenly increased, Day 35 and Day 43, and then decreased to steady-state levels. During both upset periods o-xylene removal in the 50 mg/ℓ unit remained relatively constant. In general, the PAC reactor appeared relatively unaffected by the upset conditions which caused reduced o-xylene removals in the control reactor.

11.6 EFFECT OF SOLIDS RETENTION TIME ON OVERALL TOXICS REMOVAL

Previous studies evaluating PAC addition to activated sludge have reported that combinations of high solids retention times and low PAC doses provided enhanced removal of overall organics, as measured by TOC, COD, or BOD. Activated sludge studies, described in Section 10, evaluating the effect of solids retention time on the biodegradation of the toxic organic compounds found no variation in overall removal at SRT values between 3 and 12 days. This study was conducted to evaluate the effect of SRT on the overall removal, biodegradation and/or adsorption, of both biodegradable and non-biodegradable compounds in PAC bioreactors receiving influent PAC doses of 25 and 50 mg/ℓ.

11.6.1 Non-biodegradable Compounds

11.6.1.1 Lindane

Initial studies evaluating the effect of solids retention time on the overall removal of the toxic organic compounds from PAC bioreactors were conducted with the non-biodegradable, non-volatile compound,

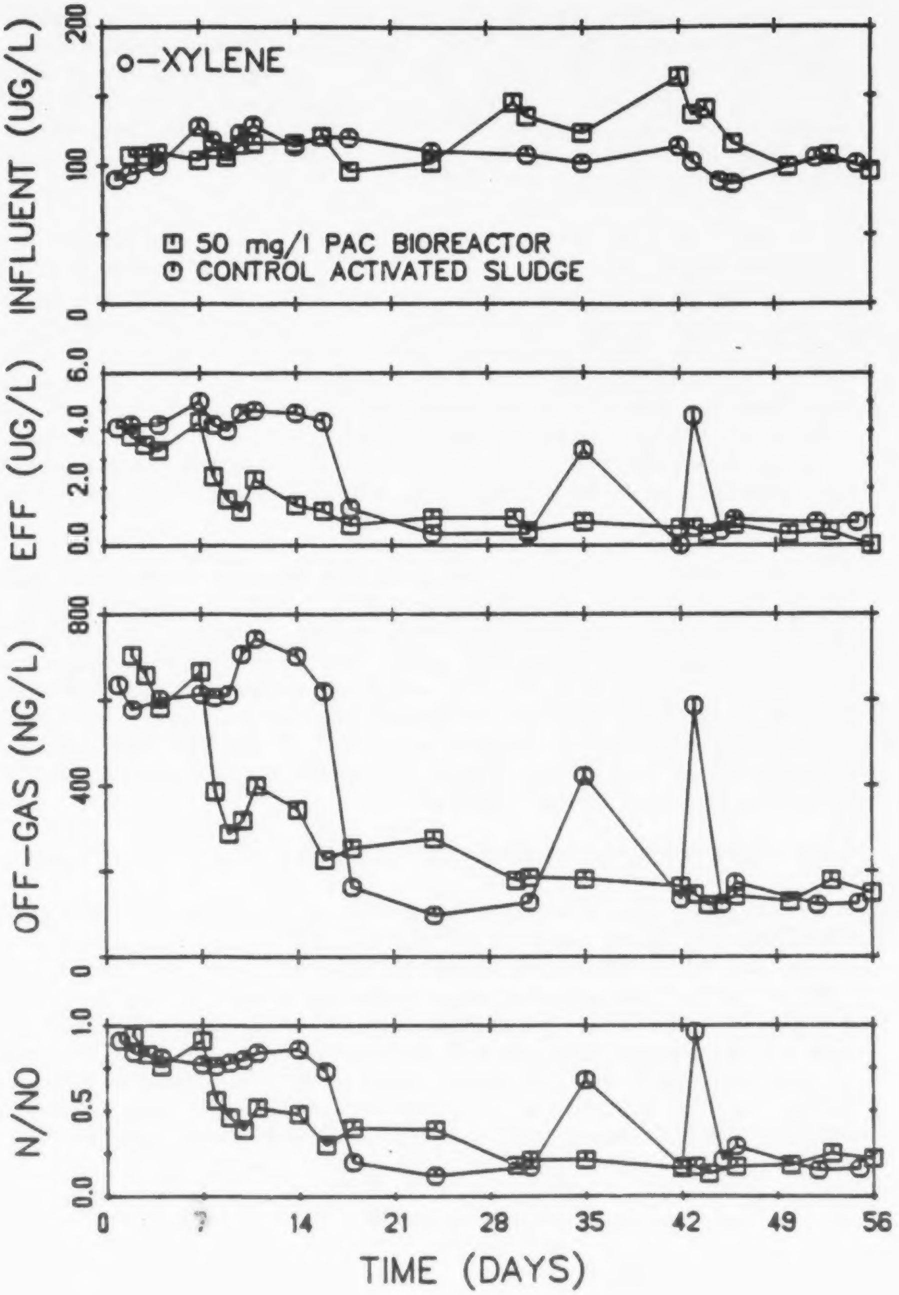


FIGURE 11-61. Effect of a 50 mg/l influent PAC dose on effluent and off-gas o-xylene concentrations and fractional recoveries, N/No.

lindane. Influent lindane and Hydrodarco C concentrations of 100 µg/ℓ and 25 mg/ℓ, respectively, were added to PAC bioreactors operated at 3, 6, and 9-day solids retention times. Results given by Figures 11-62 and 11-63 demonstrated that no significant variation in lindane removal occurred over the range of SRT's considered. Lindane removals during the eight week studies averaged 84% in the 3-day SRT unit and 83% in both the 6 and 9-day SRT bioreactors. Complete summaries of results from the three SRT PAC bioreactors are given by Table 11-18.

Steady-state mixed liquor PAC concentrations ranged from nearly 350 mg/ℓ in the 3-day SRT PAC bioreactor to over 950 mg/ℓ in the 9-day SRT PAC bioreactor. While the amount of PAC in the 3 and 9-day SRT bioreactors differed by a factor of three, the amount of lindane removed was identical. Results from this study combined with those detailing the effect of influent PAC dose suggest that the removal of a non-volatile, non-biodegradable compound with a relatively constant influent concentration in an integrated activated sludge/carbon treatment system was not controlled by the mixed liquor PAC concentration, but rather was a function of the influent PAC dose.

Unlike lindane PAC bioreactor studies reported in Section 11.3 in which lindane and slurried PAC were initially added to the influents at the same time, lindane was added to influent six to ten days prior to the slurried PAC in each of the three different SRT units. The C_e/C_i values were approximately the same in each unit prior to PAC addition and ranged from 0.93 to 0.97. Day zero in Figures 11-62 and 11-63 represent the initiation of PAC addition to the units. In each case within 24 hours the C_e/C_i and effluent values dropped to approximately the same steady-state level.

The solids retention time in the 3-day SRT PAC bioreactor was increased to 15-days after 51 days of operation. Subsequent samples collected after the new steady-state mixed liquor suspended solids concentration of between 6500 and 7000 mg/ℓ (PAC mixed liquor concentration of approximately 1500 mg/ℓ) was obtained, showed no change in lindane removal.

A fourth lindane bioreactor receiving 25 mg/ℓ Hydrodarco C was operated with an approximate SRT of 0.25 days. In this unit there was no solids recycle and the solids retention time equalled the hydraulic retention time. The steady-state mixed liquor PAC concentration was 25 mg/ℓ. Lindane in this unit was not significantly different than that observed in the other SRT studies. During the eight days the 0.25 day unit was operated lindane removal averaged nearly 81%. For an influent lindane concentration that averaged 98.4 µg/ℓ, the effluent concentration ranged from 12.3 to 24 µg/ℓ and averaged 19 µg/ℓ.

11.6.1.2 1,2-Dichlorobenzene and 1,2,4-Trichlorobenzene

The effect of solids retention time on the overall removals of the volatile compounds 1,2-dichlorobenzene and 1,2,4-trichlorobenzene was

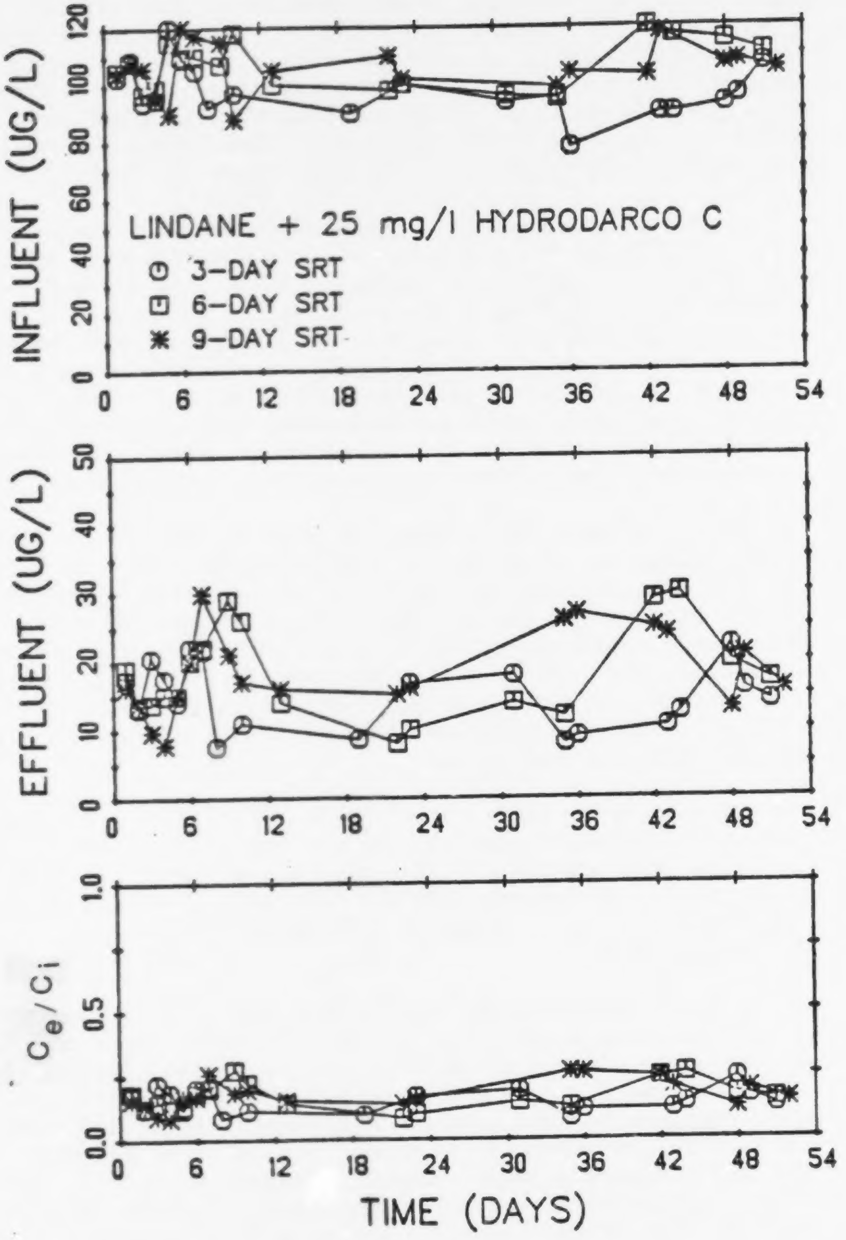


FIGURE 11-62. Effect of solids retention time on effluent lindane concentrations from 10-liter bioreactors receiving 25 mg/l influent PAC doses.

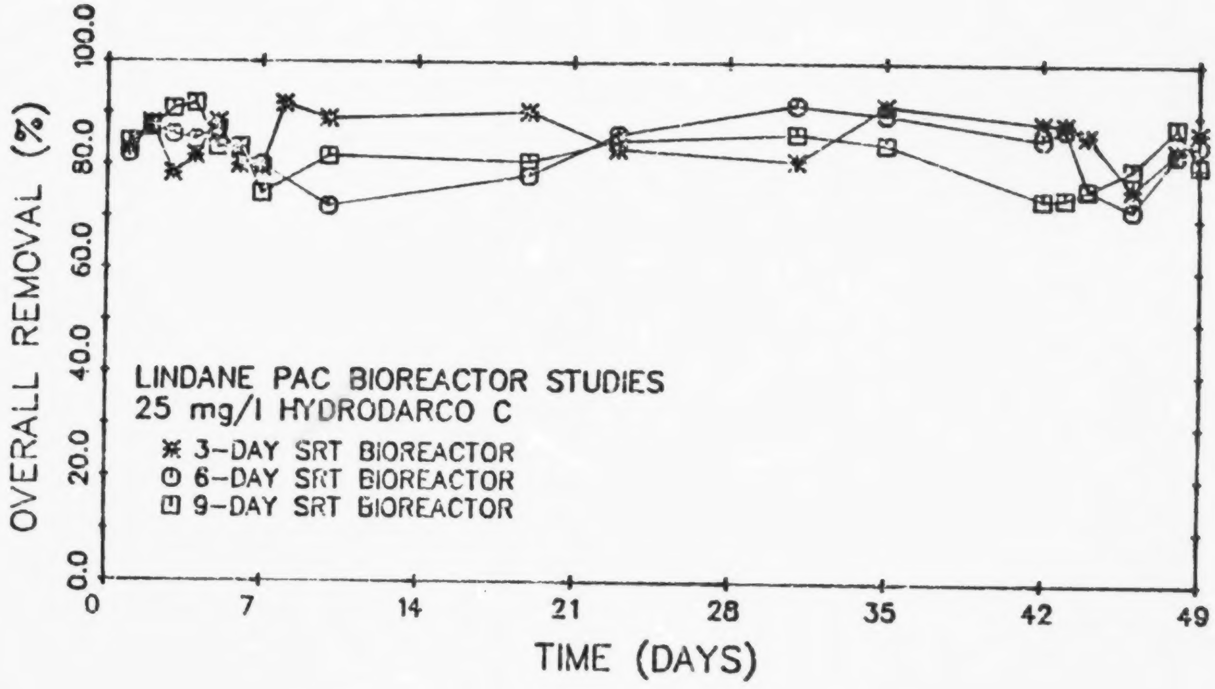


FIGURE 11-63. Effect of solids retention time (SRT) on lindane removal due to PAC adsorption in 10-liter bioreactors receiving 25 mg/l influent PAC doses.

TABLE 11-18

EFFECT OF SOLIDS RETENTION TIME ON THE REMOVAL OF LINDANE FROM BIOREACTORS RECEIVING 25 mg/ℓ HYDRODARCO C

	Solids Retention Time		
Parameter	3-Days	6-Days	9-Days
Influent (μg/ℓ)+	96.9	101	106
Effluent (μg/ℓ)+	15.2	18.4	18.7
Removal (Percent)+	84.3	82.9	82.6
MLSS (mg/ℓ)	1600	3500	4700
PAC Mixed Liquor Conc. (mg/ℓ)++	320	640	960

+ Values represent averages determined from 19 data points taken during seven weeks of bioreactor operation.

++ Theoretical values; actual concentrations averaged approximately 90% of the theoretical values.

evaluated in PAC bioreactors operated at 0.25, 3, 6, and 12-day SRT's. An influent PAC dose of 50 mg/ℓ Hydrodarco C was used for this group of studies.

Figure 11-64 graphically compares results from control activated sludge and 50 mg/ℓ PAC bioreactor studies for 1,2,4-trichlorobenzene. The slurried PAC was begun on Day 9 of the 50 mg/ℓ PAC bioreactor. Results presented in Figure 11-64 show that N/N_0 values recorded for the two units prior to PAC addition were not significantly different and were greater than 0.94, indicating complete 1,2,4-trichlorobenzene recovery. Effluent and off-gas concentrations dropped to their new steady-state levels within 24 hours after PAC addition was begun. As observed for lindane, the overall removal of 1,2,4-trichlorobenzene showed no further increase as PAC accumulated in the bioreactor mixed liquor. Approximately 60 days were required for the mixed liquor PAC concentrations to reach the steady-state concentration of 2000 to 2400 mg/ℓ. During that time effluent and off-gas concentrations remained relatively constant.

Results from the 1,2,4-trichlorobenzene 50 mg/ℓ PAC bioreactor studies conducted at 0.25, 6, and 12-day SRT's summarized by Table 11-19 show that there was no variation in overall removal as a function of solids retention time. Overall removals observed at 0.25-day SRT's were not significantly different from those recorded in the 12-day SRT study.

Results for 1,2-dichlorobenzene from 50 mg/ℓ PAC and control activated sludge studies conducted at a 12-day SRT have been graphically compared in Figure 11-65. Addition of PAC to the influent began on Day 7. Within 24 hours the effluent and off-gas concentrations had been reduced from approximately 11 μg/ℓ and 730 ng/ℓ, respectively, to steady-state values of 2 μg/ℓ and 290 ng/ℓ, respectively. As observed for 1,2,4-trichlorobenzene, no further decreases in effluent and off-gas concentrations were observed to occur as PAC accumulated in the bioreactor mixed liquor. The overall 1,2-dichlorobenzene removal recorded 24 hours after PAC addition had begun was the same as the level measured at Day 70 when the mixed liquor PAC concentration had reached a steady-state level of 1900 to 2400 mg/ℓ. The mixed liquor PAC concentration was not important for PAC bioreactors receiving a constant influent 1,2-dichlorobenzene concentration.

As shown by Figure 11-66 which graphically compares results from 50 mg/ℓ PAC bioreactors operated at 6 and 12-day SRT's, there was no difference in bioreactor performance with respect to 1,2-dichlorobenzene removal at 6 and 12-day SRT's. The influents were initially spiked with 1,2-dichlorobenzene on Day zero in both studies while slurried PAC addition was begun on Day zero in the 6-day SRT unit and Day 7 in the 12-Day SRT unit. Table 11-19 compares results from 0.25, 3, 6, and 12-day SRT bioreactor studies with an influent PAC dose of 50 mg/ℓ. As observed for 1,2,4-trichlorobenzene and lindane, there was no variation in 1,2-dichlorobenzene removal as a function of SRT over the 0.25 to 12-day range considered by this project.

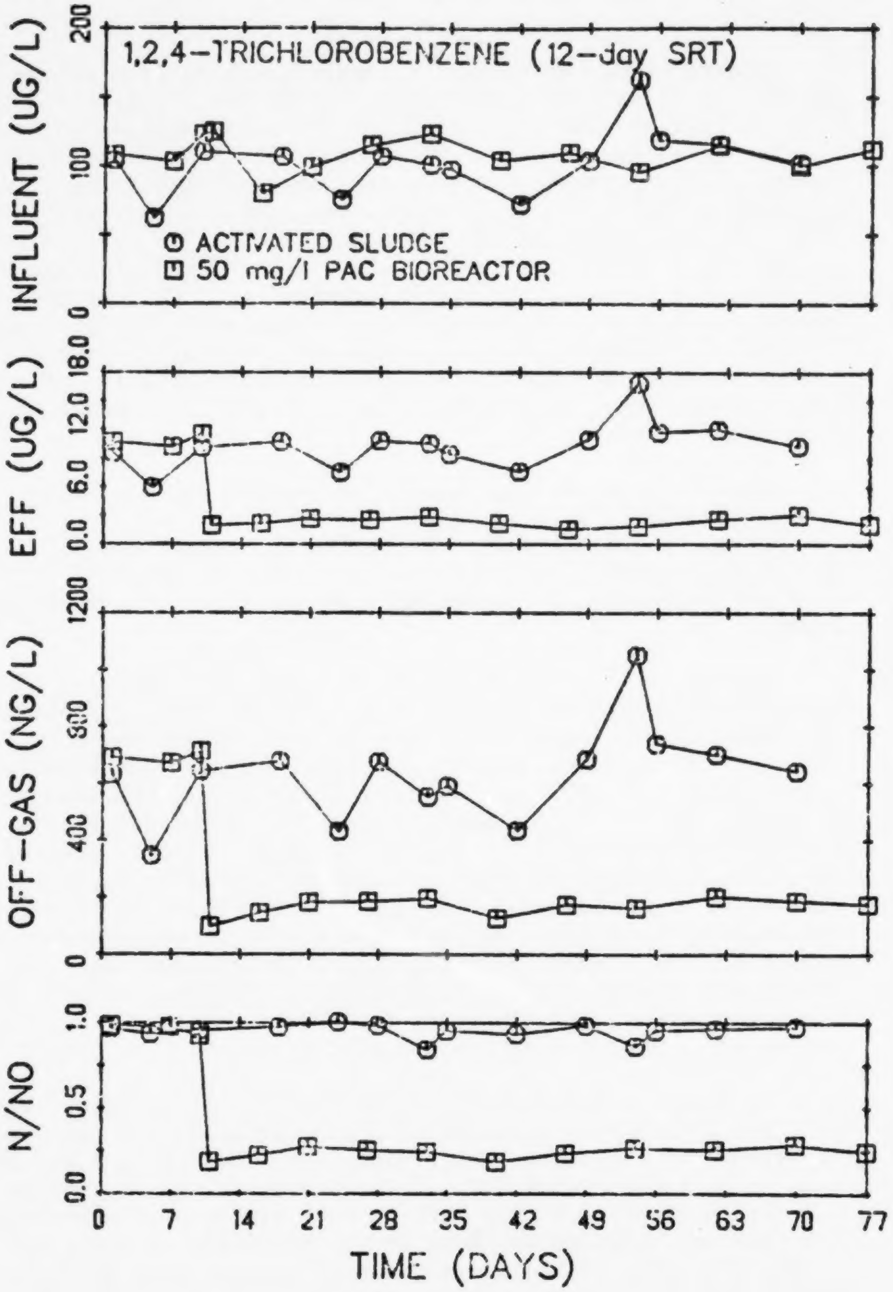


FIGURE 11-64. Effect of a 50 mg/l influent PAC dose on 1,2,4-trichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during 12-day SRT bioreactor studies. (PAC addition was begun on Day 9)

TABLE 11-19

EFFECT OF SOLIDS RETENTION TIME ON
REMOVAL OF 1,2,4-TRICHLOROBENZENE AND 1,2-DICHLOROBENZENE
IN 50 mg/1 PAC BIOREACTORS

Solids Retention Time (days)	Influent (ug/1)	Effluent (ug/1)	Off-Gas (ng/1)	Removal (%)
1,2,4-TRICHLOROBENZENE				
0.25	73	1.3	110	78.2
6	103	2.1	145	77.0
12	106	2.2	164	76.4
1,2-DICHLOROBENZENE				
0.25	95	1.8	192	76.0
3	101	2.3	180	74.1
6	115	2.9	201	71.0
12	107	2.1	170	76.5

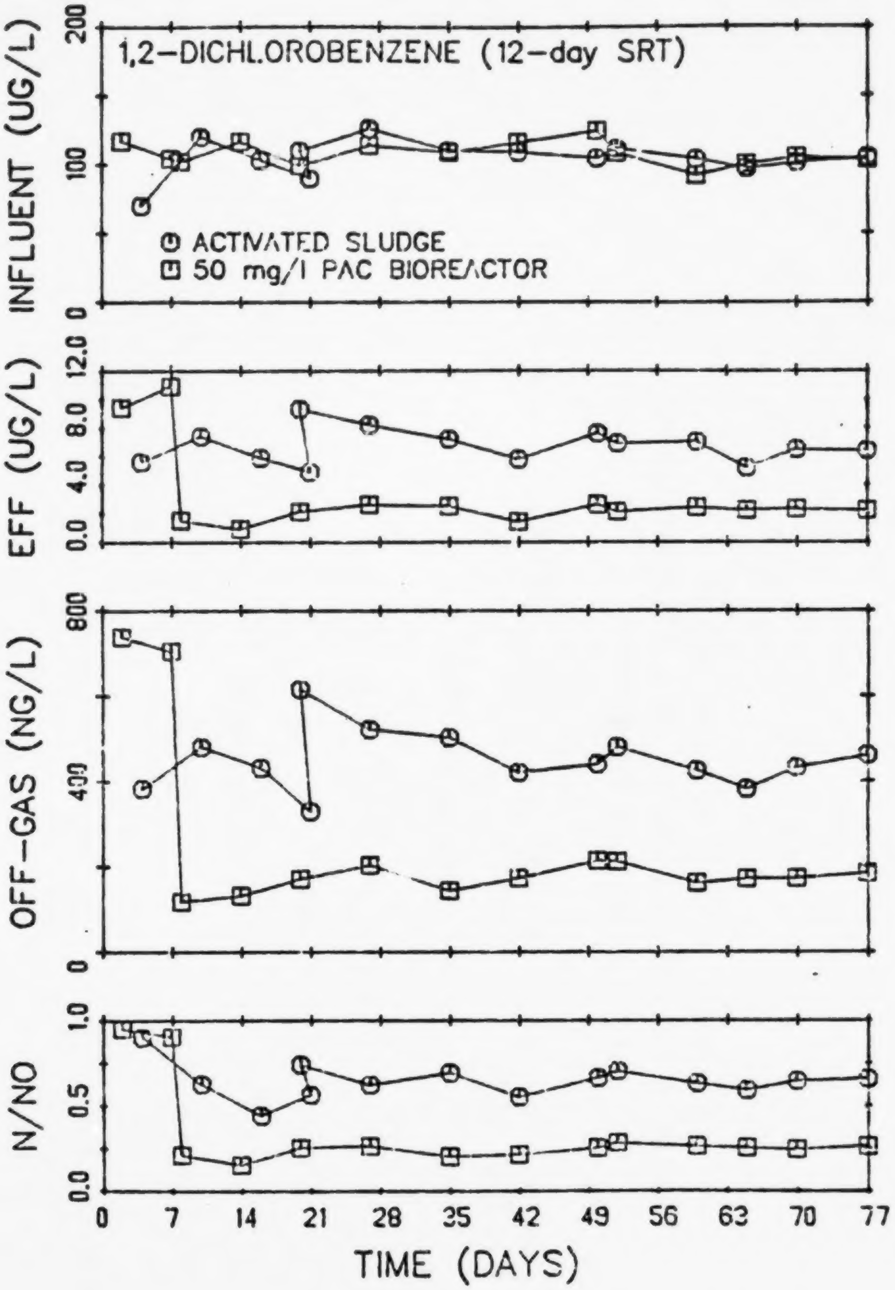


FIGURE 11-65. Effect of a 50 mg/l influent PAC dose on 1,2-dichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during 12-day SRT bioreactor studies. (PAC-addition was begun on Day 7)

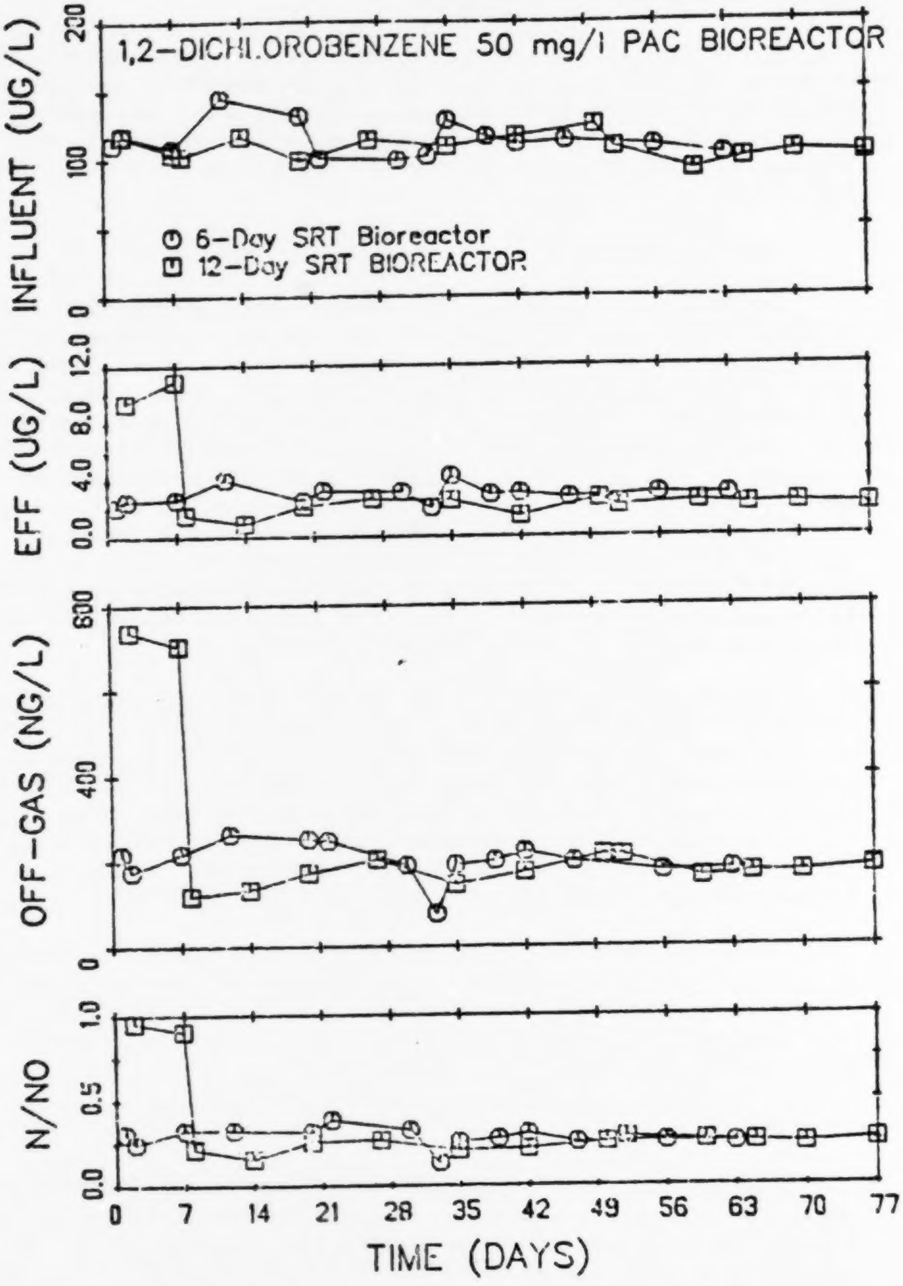


FIGURE 11-66. Comparison of effluent and off-gas concentrations and fractional recoveries, N/No, measured during 1,2-dichlorobenzene PAC-bioreactor studies with 6 and 12-day solids retention times. (Influent PAC dose was 50 mg/1.)

11.6.2 Biodegradable Compounds

The effect of SRT on the steady-state overall removals of the two volatile, biodegradable compounds benzene and chlorobenzene was evaluated in bioreactors receiving influent PAC (Hydrodarco C) concentrations of 50 mg/ℓ. Benzene and chlorobenzene 50 mg/ℓ PAC bioreactor studies were conducted at two solids retention times, 6 and 12 days.

11.6.2.1 Benzene

Activated sludge bioreactor studies demonstrated that the overall benzene removal due to biodegradation was not significantly different over the 6 to 12-day SRT range. Results from a 50 mg/ℓ PAC bioreactor operated in parallel with a control activated sludge unit, both operated with 6-day SRT's, showed that the addition of 50 mg/ℓ Hydrodarco C to the influent did not effect an increase in overall benzene removal compared to the control bioreactor. Since SRT had no effect upon benzene degradation and an influent PAC dose of 50 mg/ℓ did not enhance the overall benzene removal, two hypotheses were formulated: 1) a 50 mg/ℓ PAC dose to a 12-day SRT unit would not result in increased benzene removal compared to a 12-day SRT control activated sludge unit; and, 2) there would be no difference in overall benzene removal in 50 mg/ℓ PAC units operated at 6 and 12-day SRT's.

Bioreactor results shown by Figure 11-67 and Table 11-20 confirmed the above hypotheses. As shown by Figure 11-67, there were no differences in effluent and off-gas concentrations from a control activated sludge and a 50 mg/ℓ PAC bioreactor operated at 12-day solids retention times. Each study was conducted for ten weeks. Slurried PAC and benzene were first introduced into each unit on Day zero. The overall steady-state benzene removal averaged 84% in the activated sludge bioreactor and 87% in the 50 mg/ℓ PAC bioreactor, respectively.

There was no significant difference in overall benzene removal in 50 mg/ℓ PAC units operated at 6 and 12-days solids retention times. Overall steady-state benzene removals in the 6 and 12-day SRT units receiving 50 mg/ℓ averaged 84% and 87%, respectively. An overall summary of results for benzene is presented in Table 11-20.

11.6.2.2 Chlorobenzene

Similar rates and extents of chlorobenzene biodegradation were observed to occur in activated sludge bioreactors operated at 6 and 12-day SRT's, as described in Section 10. Results from 6-day SRT control activated sludge and 50 mg/ℓ PAC bioreactors previously described in Section 11 showed that there was no significant difference in overall chlorobenzene removal in the two units.

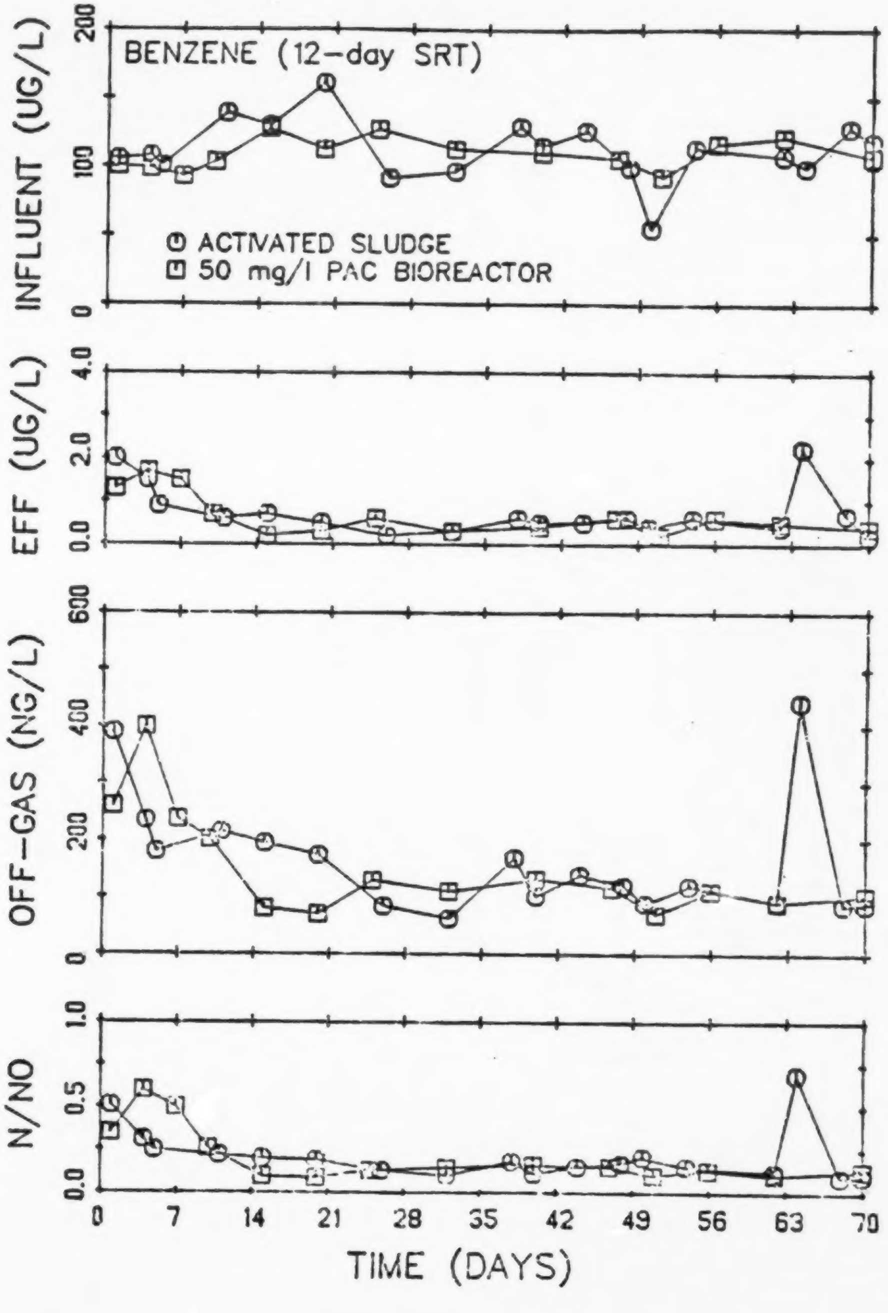


FIGURE 11-67. Effect of a 50 mg/l influent PAC dose on benzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during 12-day SRT bioreactor studies.

TABLE 11-20

EFFECT OF SOLIDS RETENTION TIME ON THE REMOVAL OF BENZENE IN 50 mg/ℓ PAC BIOREACTORS

PAC Dose (mg/ℓ)	Influent (μg/ℓ)	Effluent (μg/ℓ)	Off-Gas (ng/ℓ)	N/N_o	Overall Removal (%)
		6-DAY SRT			
Control	118(8)*	0.8(0.4)	141(40)	0.169(0.052)	83 (5)
50	106(8)	0.7(0.3)	119(21)	0.163(0.024)	84 (2)
		12-DAY SRT			
Control	113(24)	0.5(0.2)	116(41)	0.164(0.041)	84 (4)
50	123(18)	0.5(0.1)	108(15)	0.126(0.021)	87 (2)

*() is standard deviation

A 50 mg/ℓ PAC bioreactor was operated at a 12-day solids retention time for a total of ten weeks. Results from this study have been plotted with results from the 12-day SRT control activated sludge unit in Figure 11-68. Both units experienced an approximate two week acclimation phase preceding steady-state chlorobenzene removal. Overall steady-state chlorobenzene removals averaged 82% and 87% in the activated sludge and 50 mg/ℓ PAC units, respectively.

There were no significant differences in bioreactor performance with respect to chlorobenzene removal in 50 mg/ℓ PAC bioreactors operated at 6 and 12-day solids retention times, as shown by Figure 11-69. Steady-state effluent and off-gas concentrations averaged 0.8 µg/ℓ and 134 ng/ℓ, respectively, in the 6-day SRT study compared to 0.4 µg/ℓ and 104 ng/ℓ, respectively, in the 12-day SRT study. Overall chlorobenzene removal recorded for the 50 mg/ℓ PAC units including biodegradation and adsorption by the PAC, averaged 84% in the 6-day SRT bioreactor compared to 87% in the 12-day SRT bioreactor. This small difference in overall removals did not represent a significant increase in chlorobenzene removal.

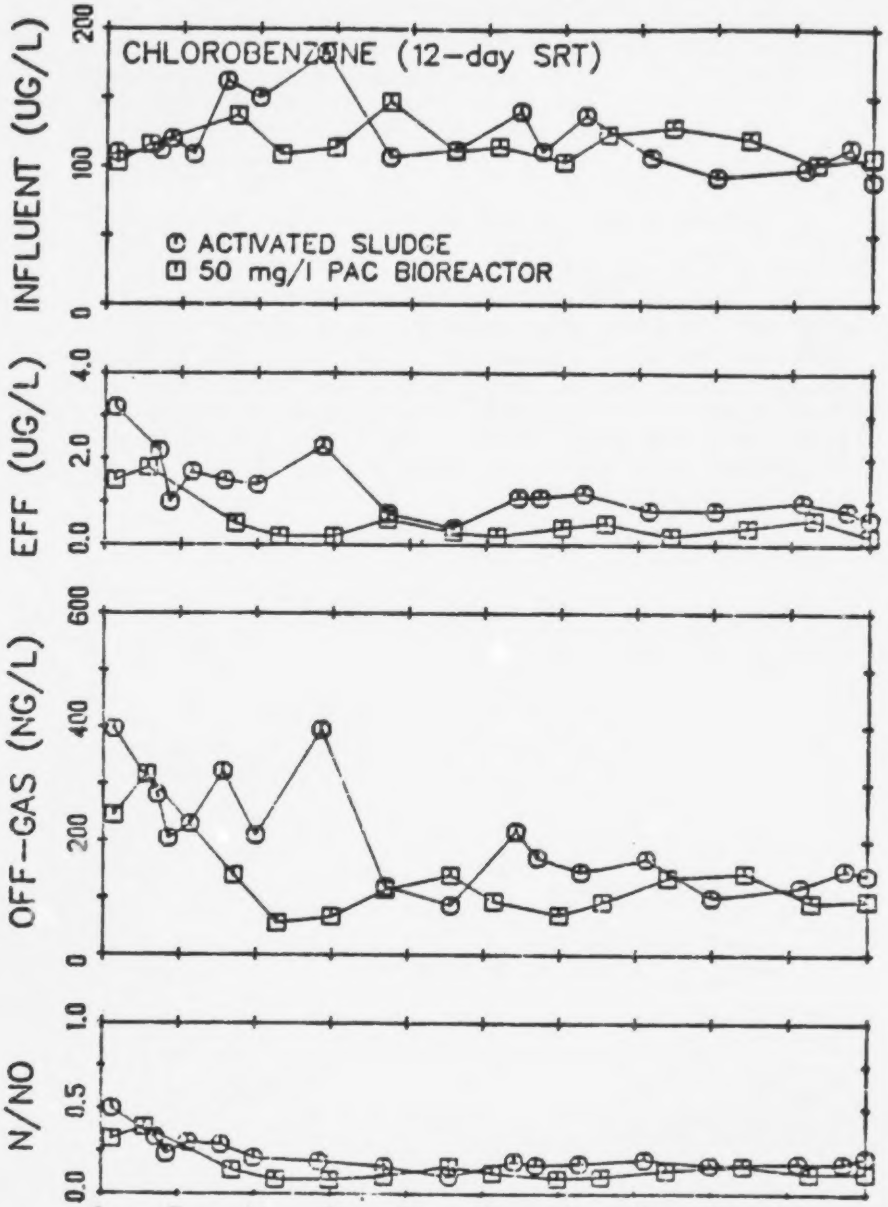


FIGURE 11-68. Effect of a 50 mg/l influent PAC dose on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during 12-day SRT bioreactor studies.

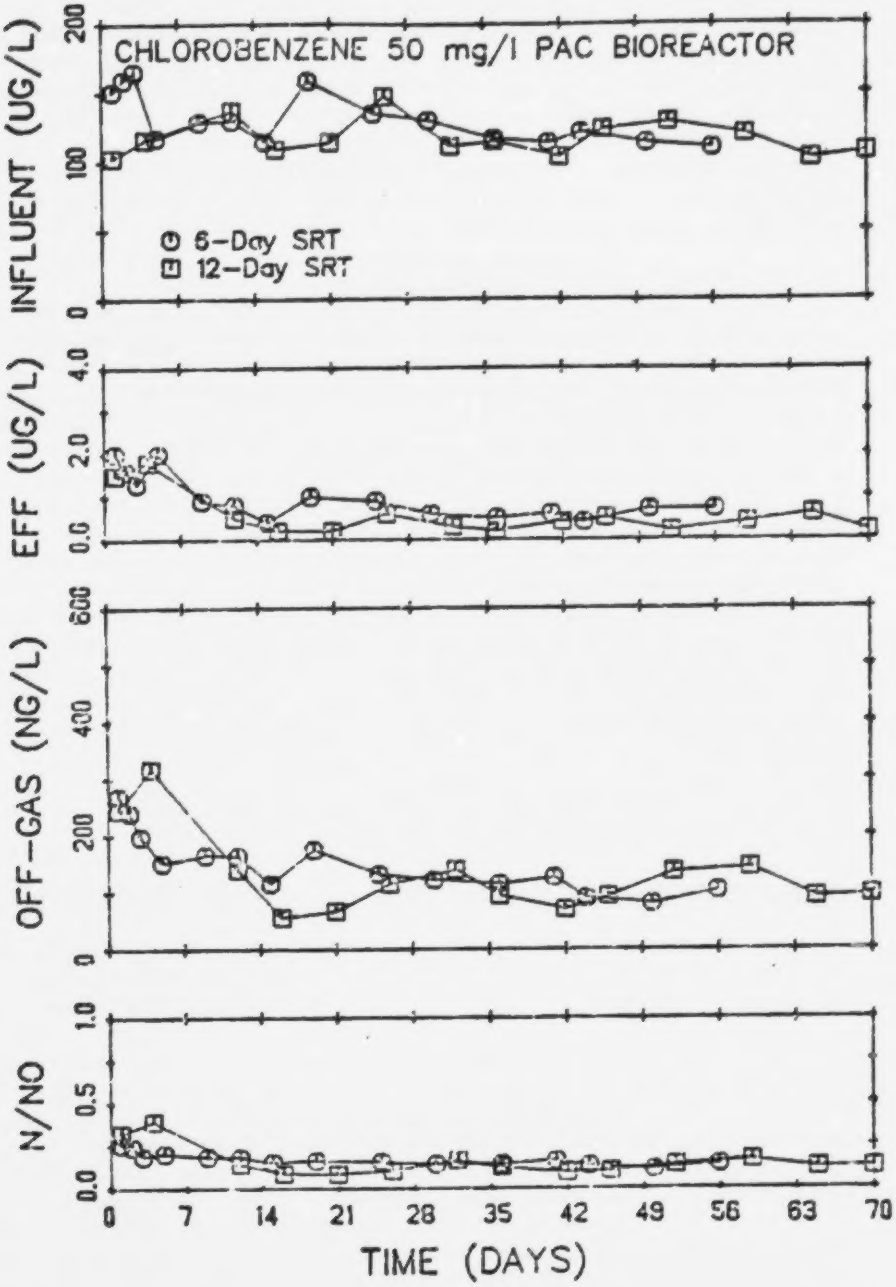


FIGURE 11-69. Comparison of chlorobenzene effluent and off-gas concentrations and fractional recoveries. N/No, measured during 50 mg/l PAC-bioreactor studies conducted with 6 and 12-day solids retention times (SRT).

11.7 EFFECT OF INTERRUPTING PAC-ADDITION ON TOXICS REMOVALS

Two studies were designed to evaluate the effect of interrupting PAC-addition to activated sludge bioreactors on the overall removals of selected biodegradable and non-biodegradable toxic organic compounds. One study was conducted in an activated sludge bioreactor receiving an influent spiked with five volatile compounds: benzene, ethylbenzene, chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene. The second study evaluated the effect of an interruption in the addition of 25 mg/l PAC to an activated sludge bioreactor receiving lindane.

11.7.1 Five Volatile Compound Study

A 100 mg/l PAC dose of Hydrodarco C was added to a bioreactor receiving synthetic wastewater influent spiked with three biodegradable compounds, benzene, ethylbenzene, and chlorobenzene; a poorly biodegradable compound, 1,2-dichlorobenzene; and a non-biodegradable compound, 1,2,4-trichlorobenzene. Influent, effluent, and off-gas concentrations of each volatile compound were monitored on a regular basis during the 84-day study. The 100 mg/l influent PAC dose was added continuously to the bioreactor for the initial 48 days of the study. After appropriate bioreactor samples were collected on Day 48, the slurried PAC feed solution was stopped and replaced with tap water to maintain the 5.5-hour hydraulic retention time. Powdered activated carbon was not added to the influent for four weeks, Day 48 to 77, resulting in a drop in the mixed liquor PAC concentration from greater than 1000 mg/l to less than 100 mg/l. On Day 77 PAC addition was continued at the original influent dose of 100 mg/l. A summary of the bioreactor operating periods is provided by Table 11-21.

TABLE 11-21
OPERATING PERIODS FOR THE 100 mg/ℓ PAC
INTERRUPTION STUDY WITH A 6-DAY SRT

Operating Period	Length (days)	Conditions
1. Days 0 to 48	48	100 mg/l PAC added continuously
2. Days 48 to 77	29	No PAC added
3. Days 77 to 84	7	100 mg/l PAC added continuously

Influent, effluent, and off-gas concentrations recorded for each compound during the 84-day study have been plotted in Figures 11-70 through 11-74. Also included in each figure are N/N_o values representing the fraction of the influent fluxes measured in effluents and off-gases combined. Overall removals of the compounds, calculated as $(1-N/N_o) \times 100$, have been compared during the 84 days in Figures 11-75 and 11-76. Average steady-state influent, effluent, and off-gas concentrations and overall removals of each compound observed during the three operating periods are given in Table 11-22. During the initial phase of the study when the influent PAC dose was 100 mg/l overall removals of the five biodegradable compounds were similar to each other. Steady-state overall removals of the five compounds averaged from Day 29 to Day 48 were approximately 90%, as detailed in

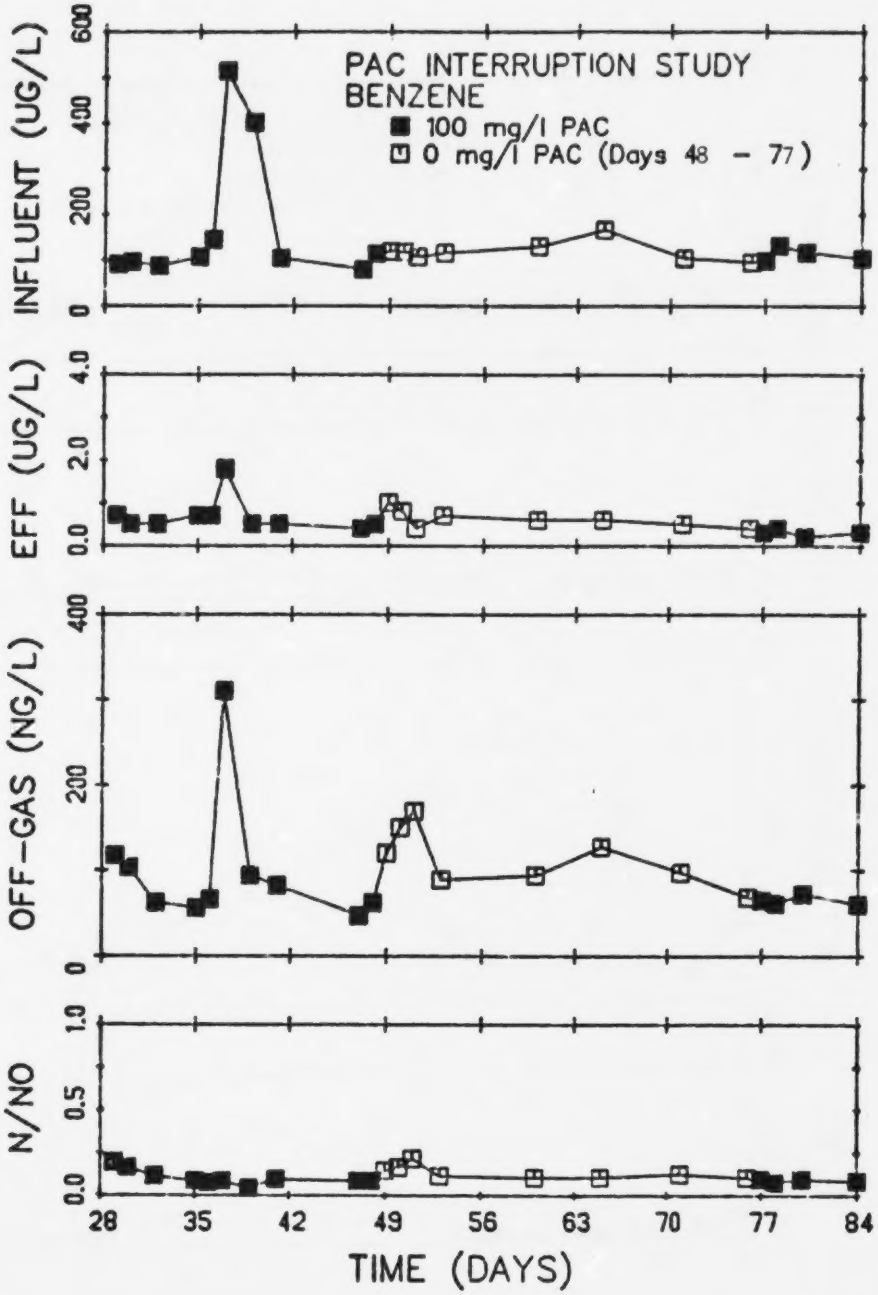


FIGURE 11-70. Effect of interrupting the addition of 100 mg/l PAC to activated sludge on benzene effluent and off-gas concentrations and fractional recoveries, N/No.

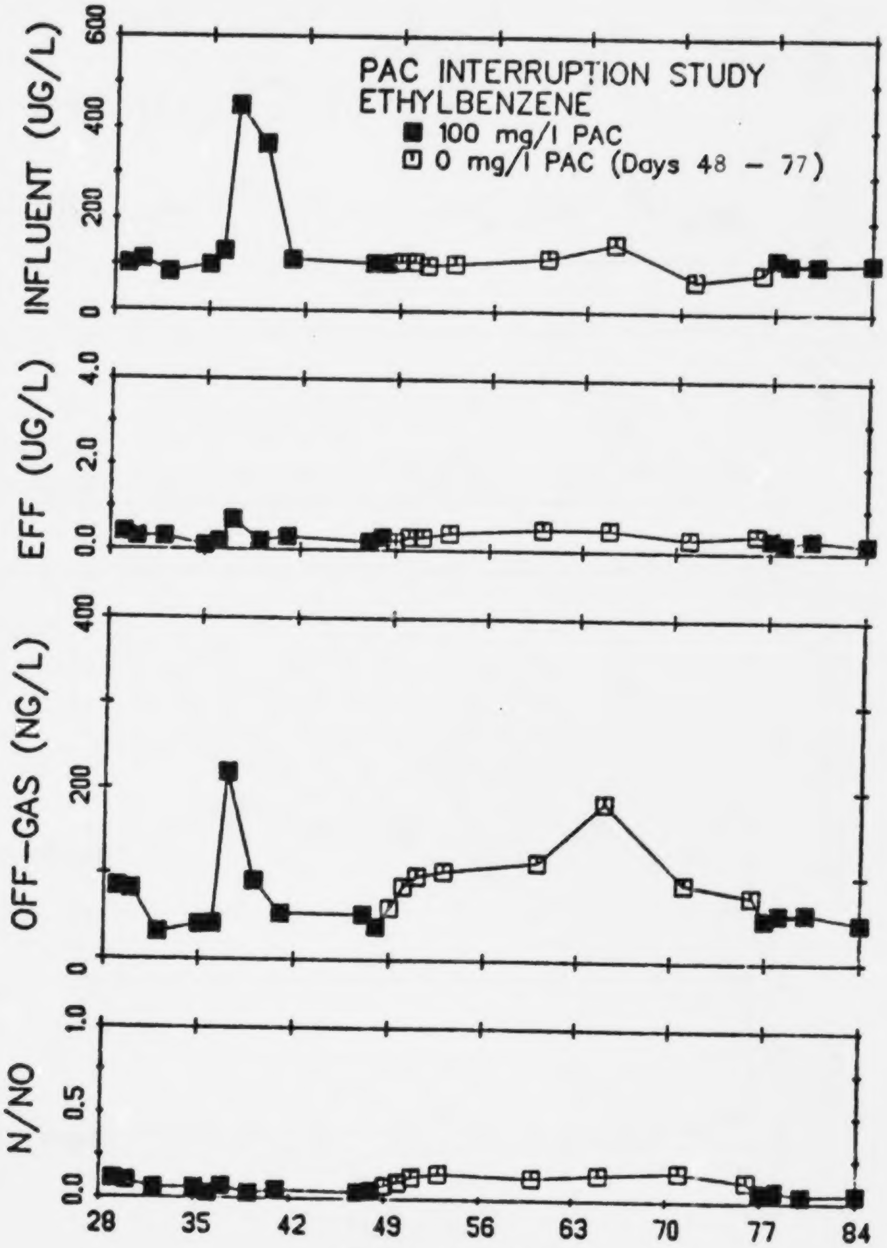


FIGURE 11-71. Effect of interrupting the addition of 100 mg/l PAC to activated sludge on ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No.

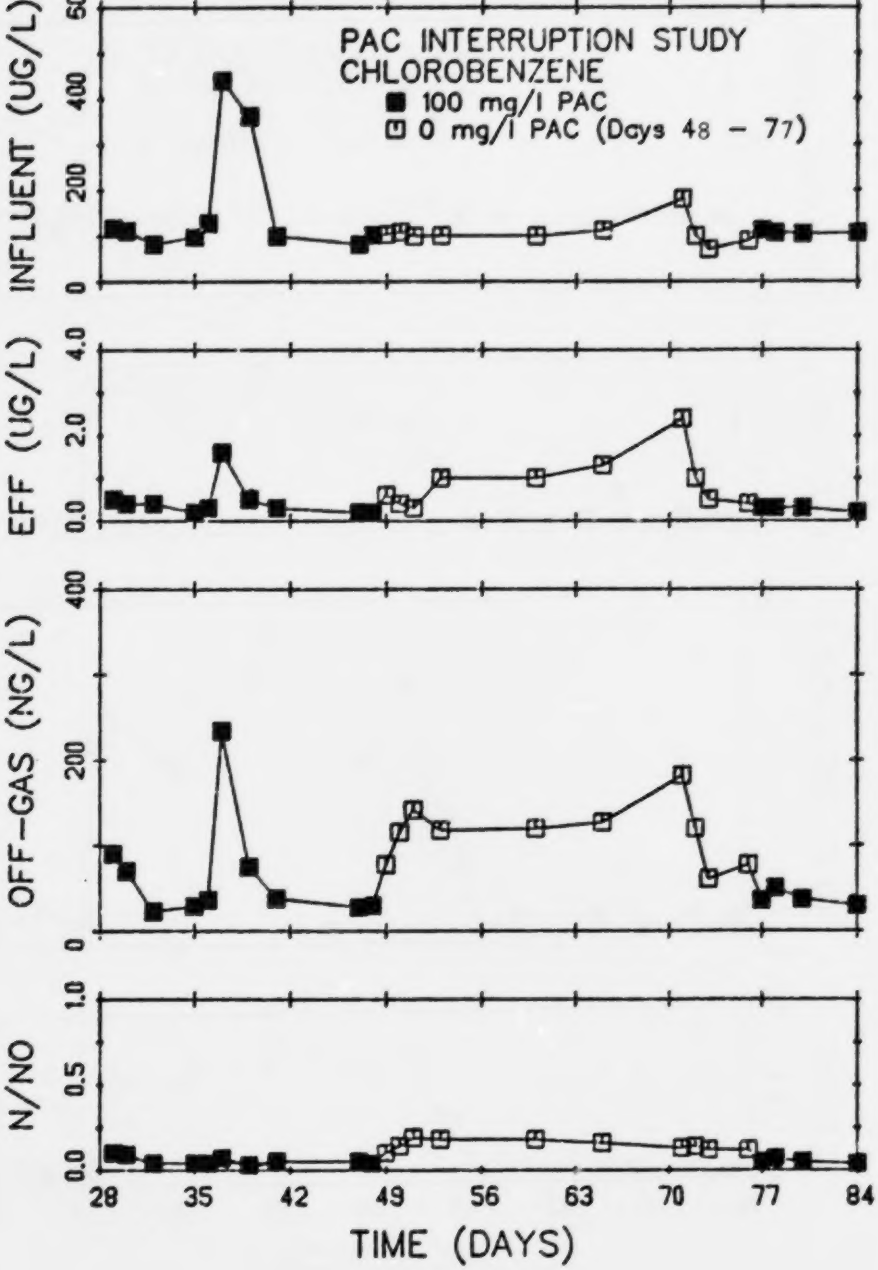


FIGURE 11-72. Effect of interrupting the addition of 100 mg/l PAC to activated sludge on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

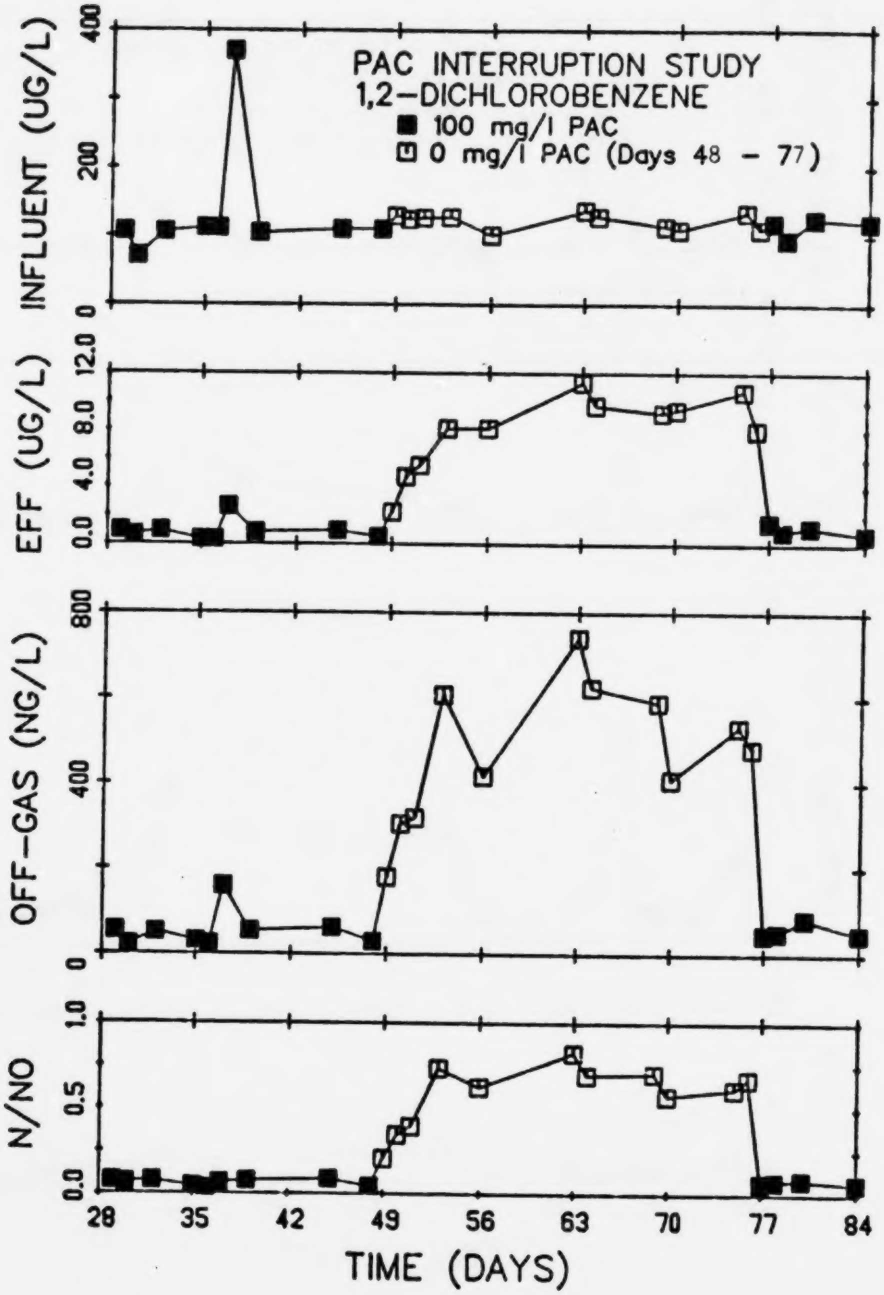


FIGURE 11-73. Effect of interrupting the addition of 100 mg/l PAC to activated sludge on 1,2-dichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/N_o.

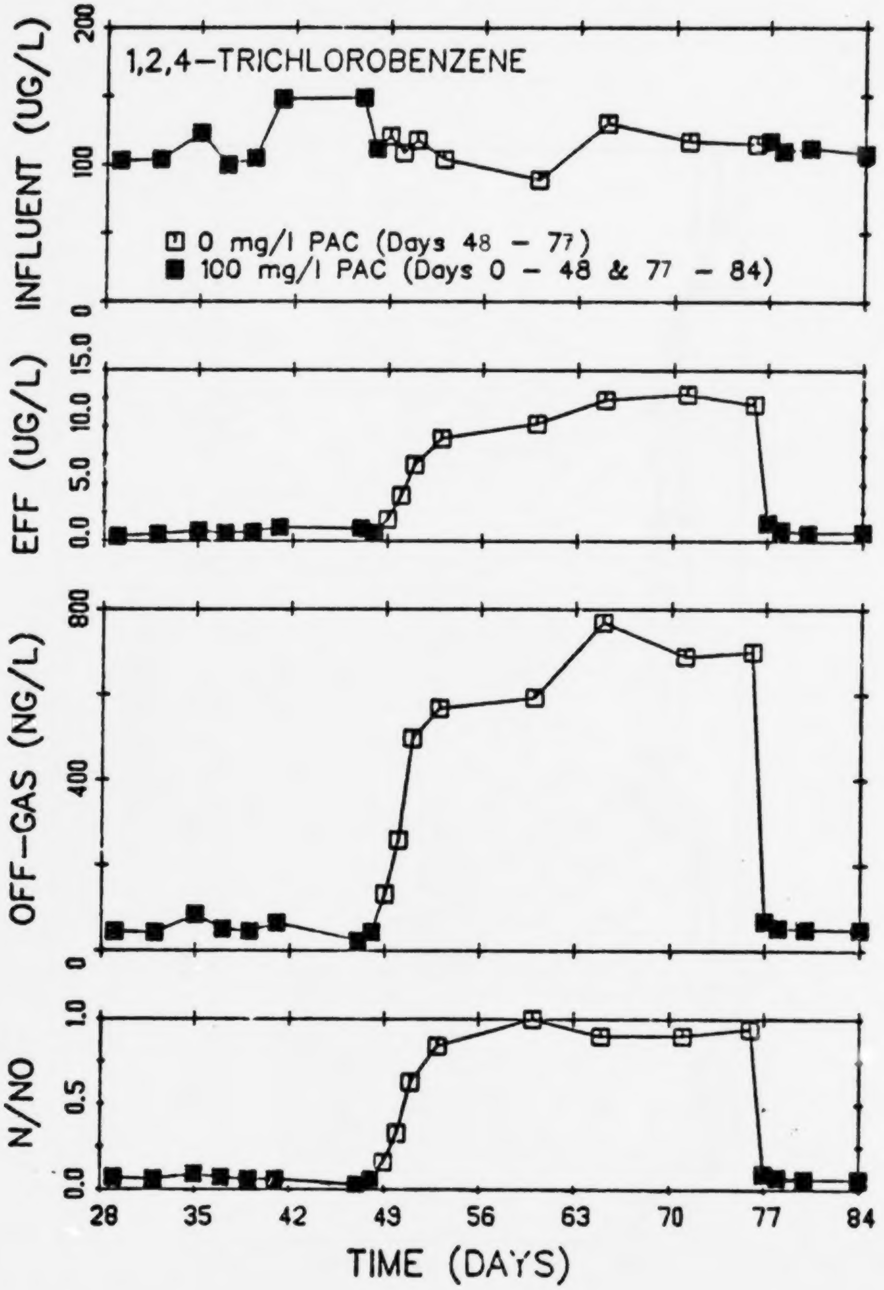


FIGURE 11-74. Effect of interrupting the addition of 100 mg/1 PAC to activated sludge on 1,2,4-trichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No.

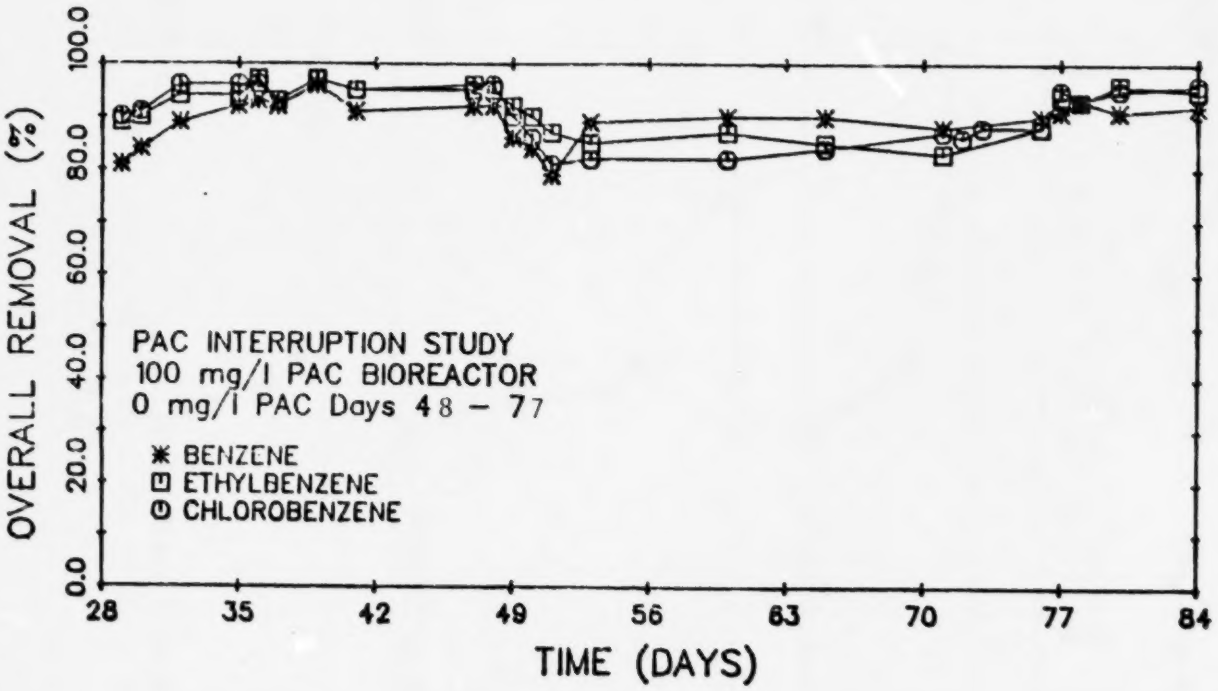


FIGURE 11-75. Comparison of benzene, ethylbenzene, and chlorobenzene overall removals due to biodegradation and adsorption measured during the PAC interruption study.

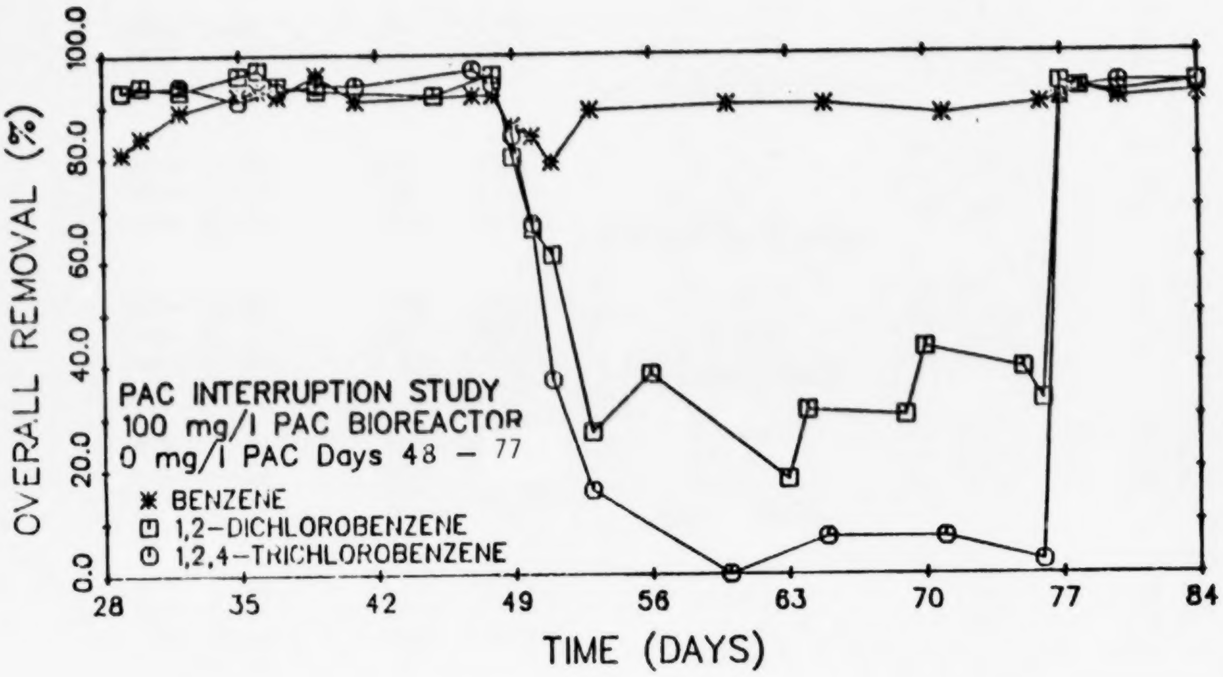


FIGURE 11-76. Comparison of benzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene overall removals due to biodegradation and adsorption measured during the PAC interruption study.

TABLE 11-22

STEADY-STATE TOXICS REMOVALS MEASURED DURING THE THREE OPERATING PERIODS OF THE PAC INTERRUPTION STUDY

Operating Period+	Influent (ug/l)		Effluent (ug/l)	Off-Gas (ng/l)	Overall Removal++ (%)
			BENZENE		
1. Days 29-48	104	(20.2)	0.6 (0.1)	74 (24)	89 (4)
2. Days 53-76	123	(27.8)	0.6 (0.1)	95 (21)	89 (1)
3. Days 77-84	114	(14.3)	0.3 (0.1)	64 (5)	92 (1)
			ETHYLBENZENE		
1. Days 29-48	106	(13.0)	0.3 (0.1)	54 (20)	94 (3)
2. Days 53-76	105	(30.5)	0.4 (0.1)	114 (42)	86 (2)
3. Days 77-84	110	(6).3)	0.3 (0.1)	53 (6)	94 (1)
			CHLOROBENZENE		
1. Days 29-48	103	(16.3)	0.3 (0.1)	43 (24)	94 (2)
2. Days 53-76	108	(30.5)	1.0 (0.6)	115 (39)	85 (3)
3. Days 77-84	108	(3.2))	0.3 (0.1)	38 (8)	95 (1)
			1,2-DICHLOROBENZENE		
1. Days 29-48	104	(13.6)	0.6 (0.3)	40 (16)	94 (2)
2. Days 53-76	120	(13.1)	9.3 (1.2)	570 (105)	32 (8)
3. Days 77-84	115	(13.3)	1.0 (0.4)	56 (17)	93 (1)
			1,2,4-TRICHLOROBENZENE		
1. Days 29-48	118	(20.1)	0.8 (0.3)	50 (18)	94 (2)
2. Days 53-76	111	(15.3)	11.3 (1.6)	664 (82))	9 (5)
3. Days 77-84	112	(3.5)	1.0 (0.4)	56 (9)	93 (1)

+ Days 29-48 100 mg/l PAC
Days 53-76 0 mg/l PAC
Days 77-84 100 mg/l PAC

++Overall Removal = $(1-N/N_0) \times 100$

( ) Standard Deviation

Table 11-22. Similar levels of overall removals were observed for each compound in single solute PAC bioreactor studies conducted with influent PAC doses of 100 mg/l, as reported in Table 11-23. These results indicate that the removal of each toxic organic compound was not adversely affected by the presence of the other compounds for the experimental conditions considered.

TABLE 11-23
STEADY-STATE REMOVALS OF TOXIC ORGANIC COMPOUNDS
FROM BIOREACTORS RECEIVING 100 mg/ℓ PAC DOSES

Compound	Overall Removal (%) Single Solute Studies	PAC Interruption Study Days 29-48
Benzene	89	90
Ethylbenzene	90	93
Chlorobenzene	92	94
1,2-Dichlorobenzene	94	94
1,2,4-Trichlorobenzene	94	93

After the steady-state overall removals of each compound were established and prior to the four week interruption in the 100 mg/l PAC dose, the influent concentration of each compound except 1,2,4-trichlorobenzene was increased from 100 ug/l to between 400 and 600 ug/l. The objective of increasing the influent concentrations was to evaluate the effect of spike loadings of toxic organic compounds on the overall removals of each compound. The increased toxics loading period occurred between Day 35 and Day 42. As results presented by Figures 11-70 through 11-74 and Table 11-24 show, the spike loadings caused only small increases in effluent and off-gas concentrations of benzene, ethylbenzene, chlorobenzene, and 1,2-dichlorobenzene. The increased influent concentrations of the four compounds had no measurable effect on either effluent and off-gas concentrations or overall removals of 1,2,4-trichlorobenzene. An interesting observation for the highly biodegradable compounds benzene, ethylbenzene, and chlorobenzene was the reduction in effluent and off-gas concentrations that occurred on the second sampling day of the spike loading period. In the case of benzene the effluent and off-gas concentrations decreased from 1.8 ug/l and 310 ng/l, respectively, to 0.5 ug/l and 94 ng/l, respectively, within two days while influent concentration was between 400 and 600 μg/ℓ. Similar results were observed for ethylbenzene and chlorobenzene.

Data collected following the cessation of PAC addition on Day 48 revealed a significant difference between the behavior of the biodegradable compounds benzene, ethylbenzene, and chlorobenzene and the poorly biodegradable and non-biodegradable compounds 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, respectively. Results for

TABLE 11-24

EFFECT OF SPIKE LOADING PERIOD ON REMOVALS OF INDIVIDUAL TOXIC ORGANIC COMPOUNDS

Operating Period	Influent (ug/l)	Effluent (ug/l)	Off-Gas (ng/l)	Overall Removal (%)
		BENZENE		
Steady-State Avg.	104	0.6	74	90
Day 37	514	1.8	310	92
Day 39	403	0.5	94	96
		ETHYLBENZENE		
Steady-State Avg.	107	0.3	54	93
Day 37	449	0.7	219	93
Day 39	365	0.2	92	97
		CHLOROBENZENE		
Steady-State Avg.	103	0.3	43	94
Day 37	440	1.6	234	93
Day 39	362	0.5	75	97
		1,2-DICHLOROBENZENE		
Steady-State Avg.	103	0.6	42	94
Day 37	370	2.6	158	94
Day 39	105	0.8	53	93
		1,2,4-TRICHLOROBENZENE		
Steady-State Avg.	118	0.8	50	93
Day 37	100	0.7	50	93
Day 39	105	0.8	45	94

1,2,4-trichlorobenzene given by Figure 11-74 show that after the PAC was omitted from the influent the PAC in the aeration section retained its ability to remove some 1,2,4-trichlorobenzene for only four to five days. During that time overall 1,2,4-trichlorobenzene removals decreased from greater than 90% to less than 10% while the mixed liquor PAC concentration decreased by approximately 50%. The effluent concentration increased from less than 1.0 ug/l to between 12 and 14 ug/l and the off-gas concentration increased from less than 100 ng/l to approximately 700 ng/l as a result of the interruption in PAC addition. At the time at which no significant removal of 1,2,4-trichlorobenzene concentration ($N/N_o \simeq 0.90$) was initially observed the mixed liquor PAC concentration was approximately 500 mg/l. The remaining PAC was in apparent equilibrium with the solution 1,2,4-trichlorobenzene (approximately 12 to 13 ug/l) and therefore not capable of adsorbing 1,2,4-trichlorobenzene in the influent. Results for 1,2,4-trichlorobenzene recorded from Day 63 to Day 77 were nearly identical to those observed in control activated sludge bioreactors. Near complete recovery of 1,2,4-trichlorobenzene was evidenced by N/N_o values between 0.90 and 1.00.

The results for 1,2-dichlorobenzene were similar to those recorded for 1,2,4-trichlorobenzene except that 1,2-dichlorobenzene recoveries, N/N_o, rose from approximately 0.10 to an average value of 0.70, indicating some microbial degradation was occurring. The 32% overall removal averaged from samples collected from Day 53-76 comparable to the 35% removals measured in control activated sludge units. Within four days after the PAC flow was stopped the effluent concentration had increased from 1.0 to 8.0 ug/l. During the period when the reactor was receiving a 100 mg/l PAC dose the effluent concentration rose from 1.0 to only 3.0 ug/l in response to the change in influent concentration from 100 to nearly 400 ug/l. In general the effluent and off-gas concentrations were extremely sensitive to changes in the influent PAC dose and relatively insensitive to changes in the influent 1,2-dichlorobenzene concentrations over the range of conditions studied.

The data collected for benzene, ethylbenzene, and chlorobenzene between Days 48 and 77 when no PAC was added were similar for each compound and different from the results for 1,2,4-trichlorobenzene and 1,2-dichlorobenzene. The results for benzene presented in Figure 11-70 show that the small increases in the effluent and off-gas concentrations which occurred during the first four days after the PAC addition was stopped were followed by a decrease in both concentrations to steady-state levels. Average steady-state benzene removal during the operating periods when the PAC influent concentration was 100 mg/l and 0 mg/l were approximately the same.

The results suggest that the activated sludge biomass had acclimated to benzene during the time 100 mg/l PAC was added to the reactor. Previous control and PAC bioreactor studies indicated that an acclimation period of approximately 14 days was required to achieve overall benzene removals in the 80% range. The benzene biodegradation rate coefficient which had been evaluated during control activated sludge studies was measured during the PAC interruption period on Day 74. The mixed liquor PAC concentration was between 100 and 200 mg/l at this point in the bioreactor study. The biodegradation rate coefficient was measured in the 10-liter bioreactor being used for the PAC interruption study with a procedure identical to that detailed in Section 5 for aerated biodegradation studies. The bioreactor was temporarily converted to a batch mode by stopping influent and sludge waste flows. An aeration rate of 4.2 l/min was used for the biodegradation study.

Results presented in the semi-logarithmic plot of concentration versus time in Figure 11-77 and summarized by Table 11-25 show a rapid removal of benzene due to biodegradation and volatilization. An overall removal rate coefficient, k_o, of 0.71 min^{-1} was measured with a correlation coefficient (r^2) of 0.999. The volatilization rate coefficient, k_v, corresponding to a 4.2 l/min aeration rate was calculated to be 0.078 min^{-1}. The difference between the overall removal rate coefficient and the volatilization rate coefficient is the biodegradation rate coefficient. This value of 0.63 min^{-1} was nearly identical to the calculated value of 0.67 min^{-1} based upon a CMF reactor mass balance using measured influent, effluent, and off-gas concentrations and assuming first order biodegradation kinetics. Pertinent information concerning the bioreactor operating conditions and measured benzene concentrations the day the biodegradation study was conducted are given in Table 11-25.

The results recorded for ethylbenzene and chlorobenzene during the 84-day study in Figures 11-71 and 11-72, respectively, were nearly identical. Small increases in effluent and off-gas concentrations of each compound occurred as a result of the increased influent concentrations between Days 35 and 42 of the spike loading period. While influent concentrations increased from 100 to 500 ug/l, effluent concentrations of ethylbenzene and chlorobenzene rose to only 0.7 and 1.6 ug/l, respectively, from their steady-state levels of approximately 0.3 ug/l.

Overall removals of both ethylbenzene and chlorobenzene decreased slightly during the first four days after the influent PAC concentration was changed from 100 to 0 mg/l. Ethylbenzene removal decreased from 94 to 86% while chlorobenzene decreased from 94 to 85%. The reduction in overall removal is evidenced in Figures 11-71 and 11-72 by the small increase in N/N_o values between Days 48 and 53. Overall removals of each compound achieved new steady-state levels within five days after the PAC addition was stopped. Results for the non-biodegradable compound 1,2,4-trichlorobenzene indicated that approximately the same length of time was required for the PAC remaining in the aeration section of the bioreactor to exhaust its capability to adsorb 1,2,4-trichlorobenzene.

One of the most interesting aspects of the PAC interruption study was the apparent acclimation of the activated sludge microorganisms to benzene, ethylbenzene, and chlorobenzene, and to a lesser extent 1,2-dichlorobenzene, prior to the PAC interruption phase. This acclimation likely occurred at the beginning of the study within the two to three weeks after the toxics were added to the influent. If the system had not acclimated to the biodegradable compounds prior to the PAC interruption phase there would have been a more significant decrease in overall removals followed by a gradual two-week increase

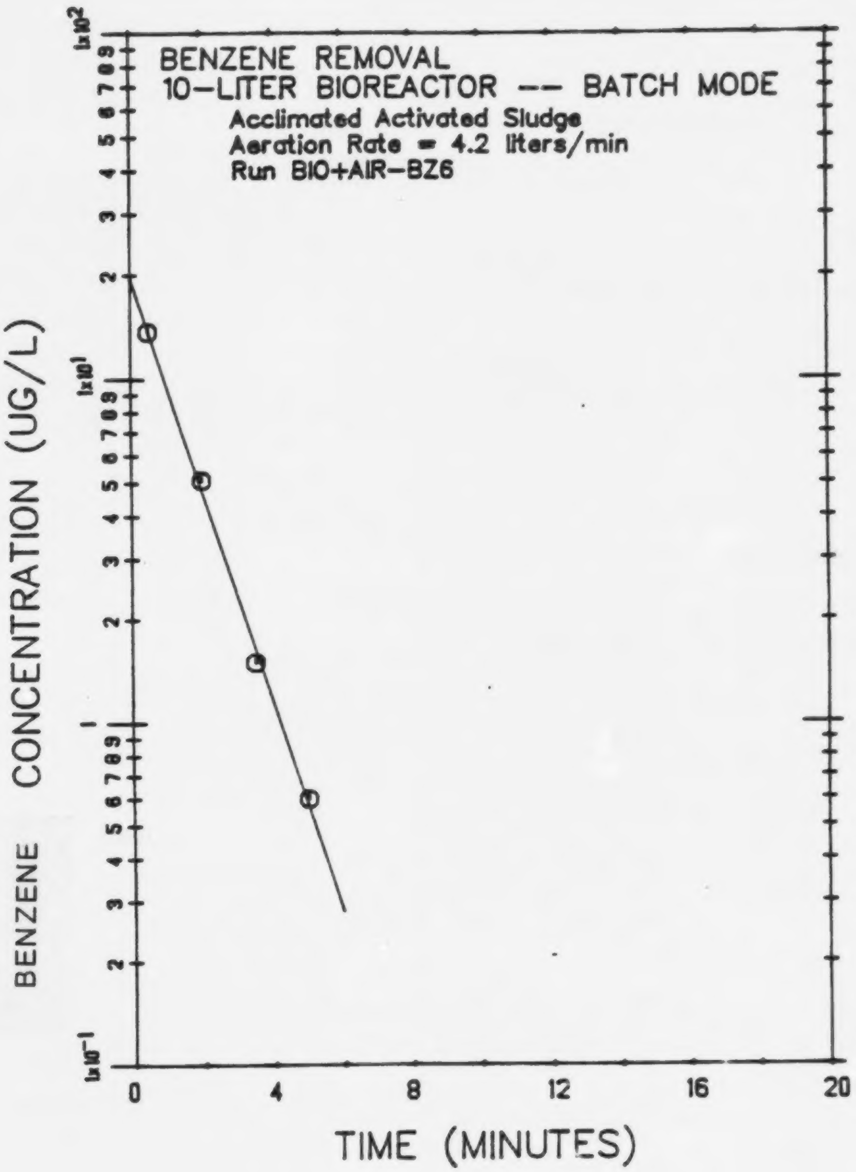


FIGURE 11-77. Experimental data and best-fit line describing benzene biodegradation by activated sludge in a completely-mixed batch rate study in a 10-liter bioreactor with a 4.2 liter/min aeration rate.

TABLE 11-25

RESULTS FROM 10-LITER CMB BIODEGRADATION RATE STUDY WITH AERATION

CMB BIODEGRADATION RESULTS

Solute: Benzene
Run: BIO + AIR - BZ6
Activated Sludge Source: Acclimated activated sludge from PAC Interruption Bioreactor, Day 74

k_o (min^{-1}): 0.707
corr. coeff.: 0.999
k_v (min^{-1}): 0.078 (Q_a = 4.2 l/min)
k_b (min^{-1}): 0.629

BIOREACTOR OPERATING SUMMARY

Influent (ug/l): 167
Effluent (ug/l): 0.4
Off-Gas (ng/l): 127
N/N_o: 0.092
Overall Removal (%): 90.8
k_v (min^{-1}): 0.065
k_b, calculated (min^{-1}): 0.673
MLSS: 3850
$\bar{t}$: 5.6
(Q_a = 3.5 l/min)

PREDICTED EFFLUENT, OFF-GAS AND OVERALL TOXICS REMOVAL USING K_b MEASURED IN CMB STUDY

Effluent (ug/l): 0.7
Off-Gas (ng/l): 134
N/N_o: 0.098
Overall Removal (%): 90.2

to steady-state levels. Instead the steady-state removals due to microbial degradation occurred within five days after the PAC-addition was stopped.

The original influent PAC dose of 100 mg/l was begun again after bioreactor samples for analyses of the toxic organic compounds were collected on Day 77. Within 24 hours effluent and off-gas concentrations of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene had decreased to the steady-state levels that existed during the initial 48 days of the study. Overall removals of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene increased from 32 to 93% and from 9 to 93%, respectively. In marked contrast to results for 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, no significant change in the overall benzene removal occurred as a result of the continuation of the 100 mg/l PAC dose. Overall removals of ethylbenzene and chlorobenzene increased slightly to steady-state levels observed with the initial 100 mg/l PAC dose. A summary of overall removals during the three operating periods is provided by Table 11-26.

11.7.2 Non-Volatile Compound

Two additional bioreactor studies were conducted with lindane to evaluate the response of the integrated activated sludge/carbon system to PAC interruption. An influent PAC dose of 25 mg/l was used in each case. Figure 11-78 presents the results from an interruption (at Day 0) in PAC feed to a bioreactor operated at a 9-day SRT and receiving an average influent lindane concentration of 80 ug/l. The average value of C_e/C_i for the reactor under steady-state conditions prior to PAC interruption was 0.16. The mixed liquor PAC continued to adsorb lindane for an additional six days before becoming exhausted. Twenty-four hours after the PAC dose was stopped the effluent concentration increased by only a small amount while after three days the effluent concentration had increased from 12 to 28 μg/ℓ. When the influent lindane concentration was increased to an average value of 250 ug/l and the solids retention time reduced to three days, effluent concentration increased more rapidly in response to the interruption in PAC addition as shown by Figure 11-79. In both studies the effluent concentration dropped to its original steady-state value within 24 hours after PAC-addition was continued.

TABLE 11-26

SUMMARY OF AVERAGE TOXICS REMOVALS FROM THE 100 mg/ℓ PAC INTERRUPTION BIOREACTOR STUDY

Compound	100 mg/l Period Day 29-48	0 mg/l Period Day 53-76	100 mg/l Period Day 77-84	Single Solute Studies	
				Control	100 mg/l PAC
Benzene	89	89	92	83	89
Ethylbenzene	94	86	95	81	90
Chlorobenzene	94	85	95	81	92
1,2-Dichlorobenzene	94	32	93	37	94
1,2,4-Trichlorobenzene	94	9	93	3	94

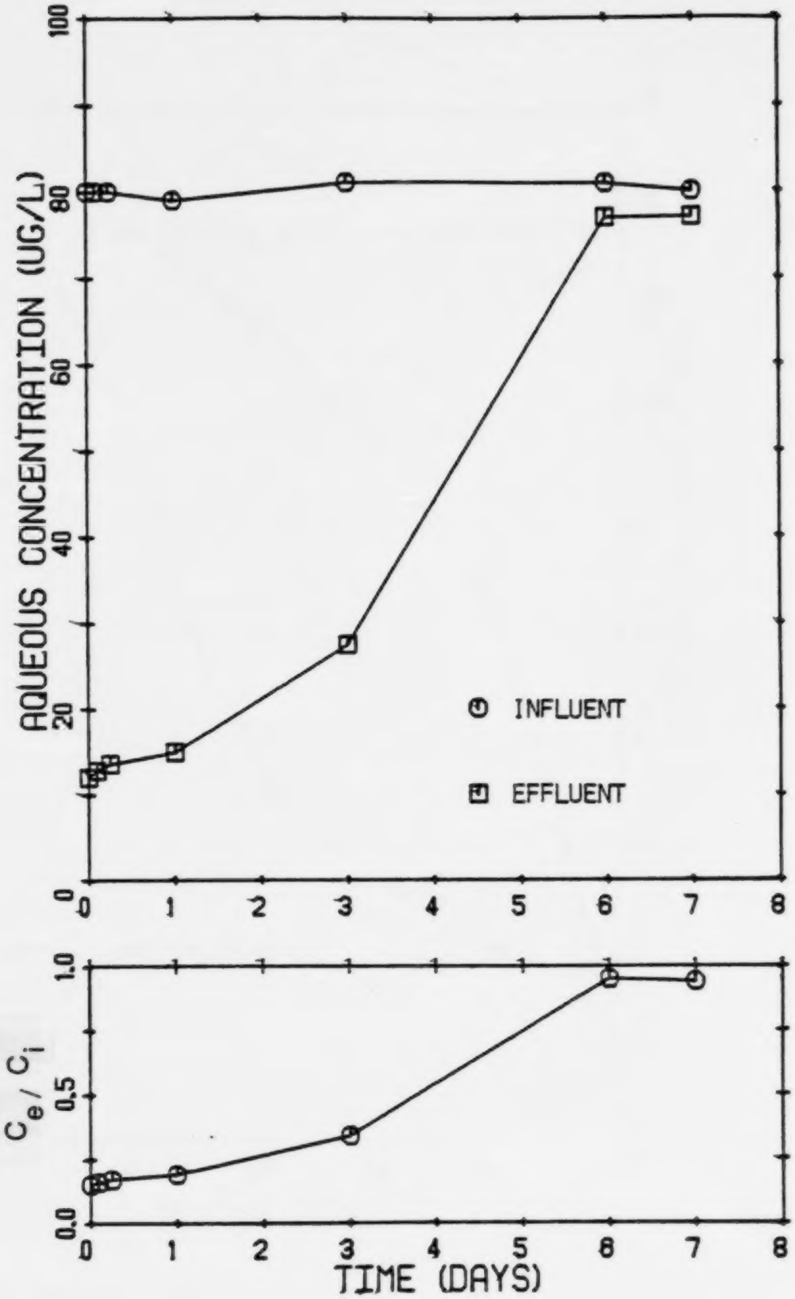


FIGURE 11-78. Effect of interrupting the addition of 25 mg/l PAC to activated sludge on lindane effluent concentration from a 10-liter bioreactor with a 9-day SRT.

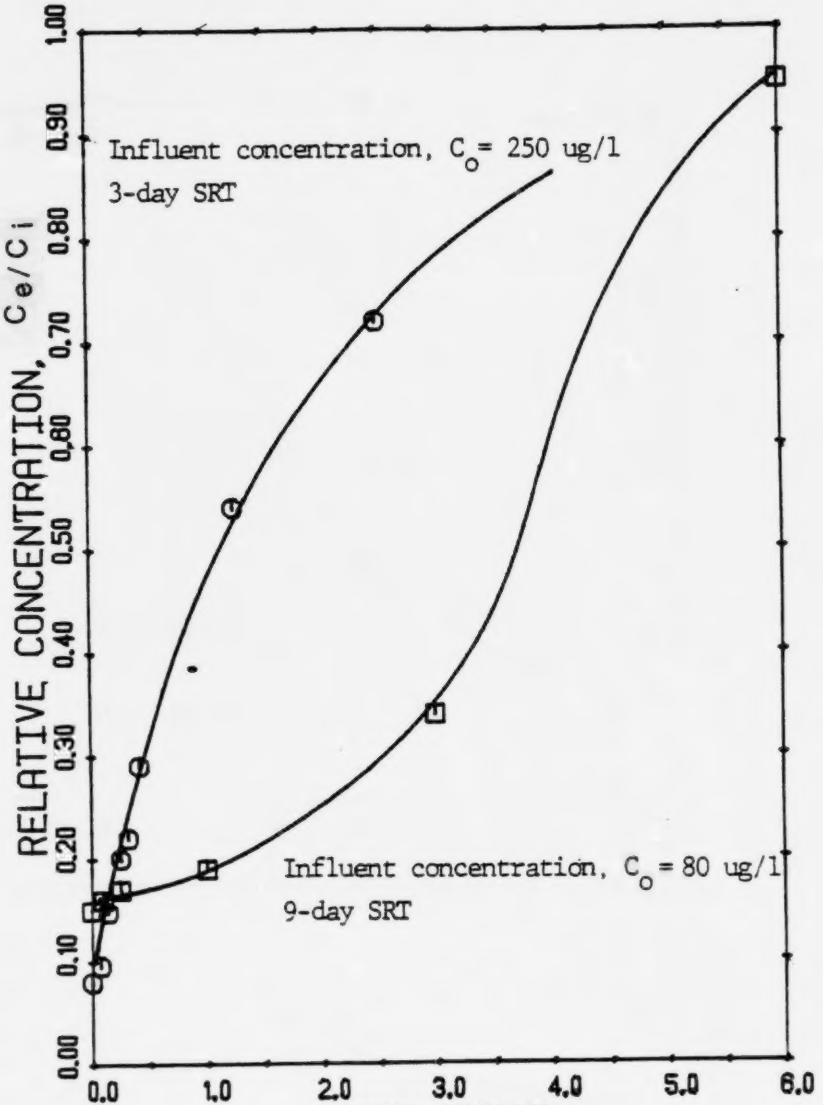


FIGURE 11-79. Effect of interrupting the addition of 25 mg/l PAC to activated sludge on lindane effluent concentrations.

11.8 TRANSIENT LOADING STUDY

An integrated activated sludge/carbon treatment bioreactor study was conducted with transient influent loadings of three toxic organic compounds: benzene, ethylbenzene, and chlorobenzene. The bioreactor received an influent PAC dose of 100 mg/l of Hydrodarco C. The three organic compounds were added on a transient loading cycle consisting of two days during which time the toxics were added to the influent followed by three days when the toxics were omitted from the influent. The transient loading study was conducted for a total of 88 days. A mean solids retention time and a hydraulic residence time of 6 days and 5.5 hours, respectively, were used throughout the study. The 100 mg/l PAC bioreactor was operated in parallel with the activated sludge transient loading bioreactor described in Section 10. Influent, effluent, and off-gas analyses typically were conducted each day of the two day period when the toxics were added to the influent flow.

Influent, effluent, and off-gas concentrations and N/N_o values have been plotted for the full 88 days of the study for benzene, ethylbenzene, and chlorobenzene in Figures 11-80, 11-81, and 11-82, respectively. During the initial 43 days of the study influent concentrations were maintained between 100 and 120 ug/l. Influent concentrations up to 600 to 750 ug/l were evaluated in the latter 46 days of the study.

The influent concentration of benzene, ethylbenzene, and chlorobenzene averaged between 100 and 120 ug/l during the first 43 days of the study. Table 11-27 summarizes results for each compound from this operating period. Results for benzene presented in Figure 11-80 show that the fractional recovery, N/N_o, initially increased from 0.30 to nearly 0.50 during the first week before decreasing to a steady-state value of 0.16 after approximately three weeks. The overall benzene removal increased, therefore, during the initial three weeks from between 50 to 70% to a steady-state level of 84%. Decreases in both effluent and off-gas concentrations contributed to the observed increase in benzene removal. This increased removal was a result of increased microbial degradation of benzene. Similar acclimation phases were observed in nearly all activated sludge and PAC bioreactor studies conducted with benzene. PAC bioreactor studies with non-degradable compounds, lindane and 1,2,4-trichlorobenzene, demonstrated that toxics' removals due solely to carbon adsorption reached steady-state levels within 24 hours after initiation of PAC addition. Results from the 100 mg/l PAC transient loading study were not significantly different from those observed in the benzene steady-state loading study with a 100 mg/l PAC dose, as shown by the comparison in Figure 11-83. Steady-state benzene removals in the steady-state and transient loading studies averaged 86% and 84%, respectively. The transient nature of benzene addition to the 100 mg/l PAC bioreactor had no measurable affect on the system's ability to remove benzene.

Results recorded for ethylbenzene during the initial 43 days of the transient loading study are presented by Figure 11-81. Steady-state ethylbenzene removal was achieved within 24 hours after 100 mg/l of the slurried PAC dose was initially added to the bioreactor. Effluent and off-gas concentrations averaged 0.8 ug/l and 128 ng/l,

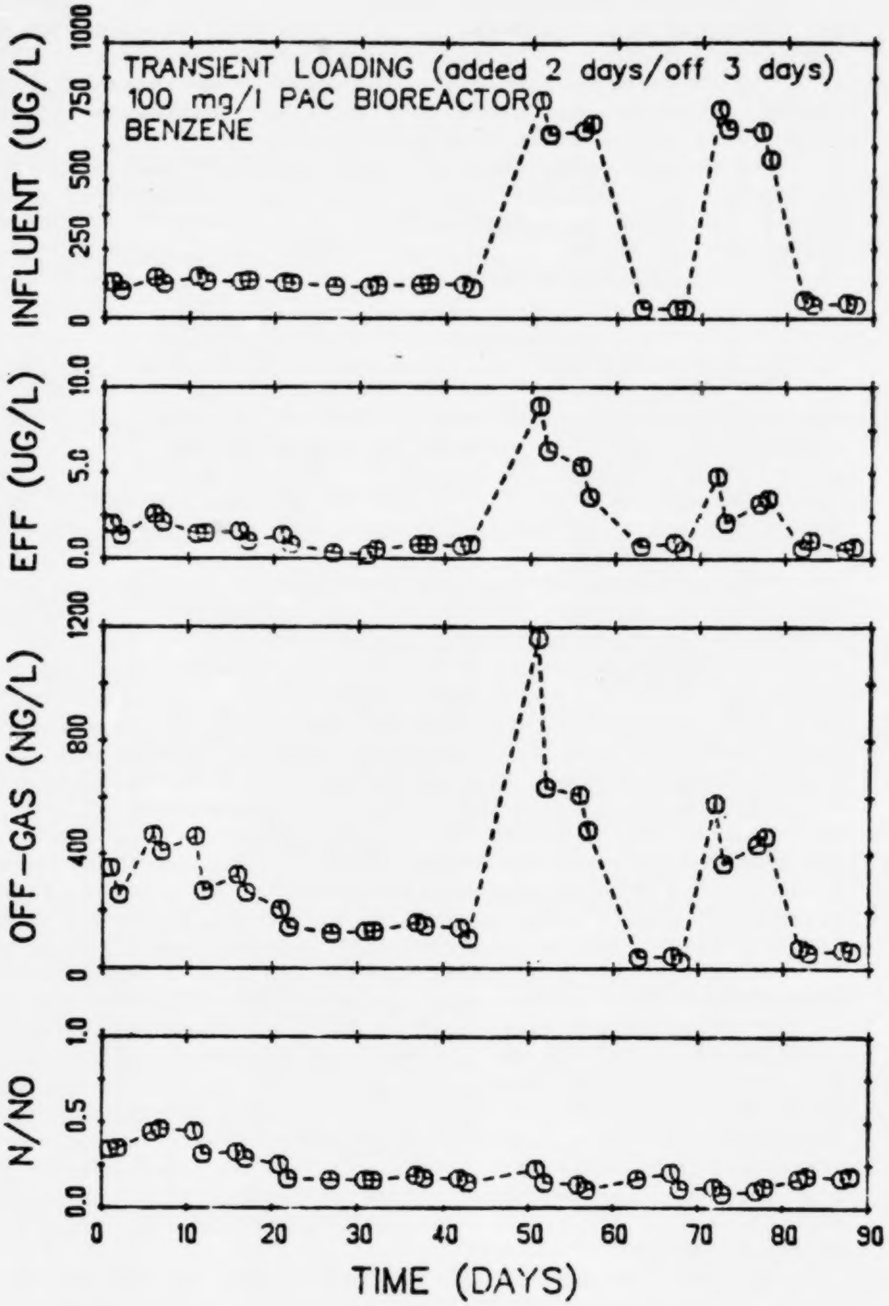


FIGURE 11-80. Benzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during a 100 mg/l PAC-bioreactor study with transient toxics loadings. (2 days added to influent/3 days omitted)

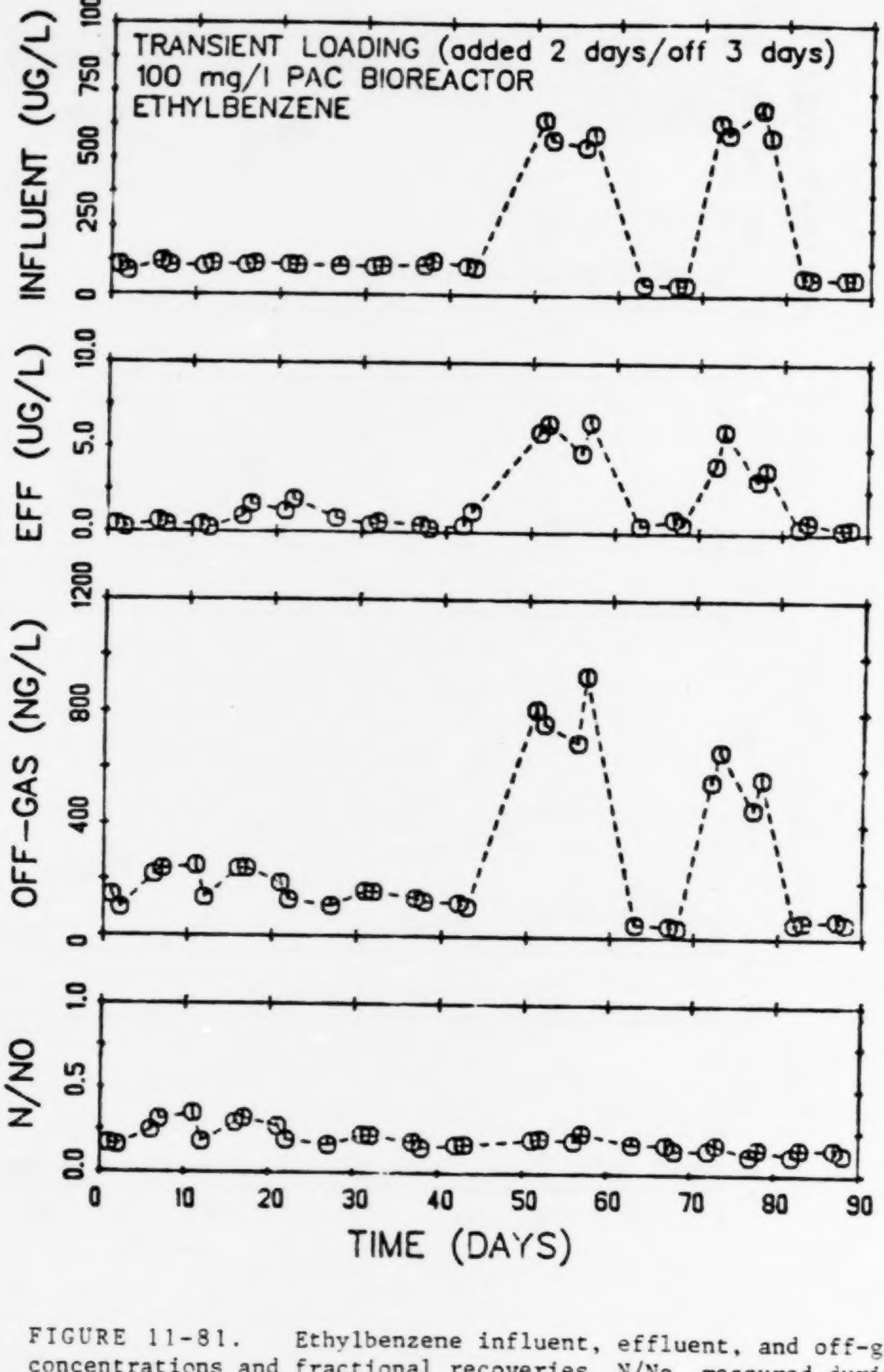


FIGURE 11-81. Ethylbenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during a 100 mg/l PAC-bioreactor study with transient toxics loadings. (2 days added to influent/3 days omitted)

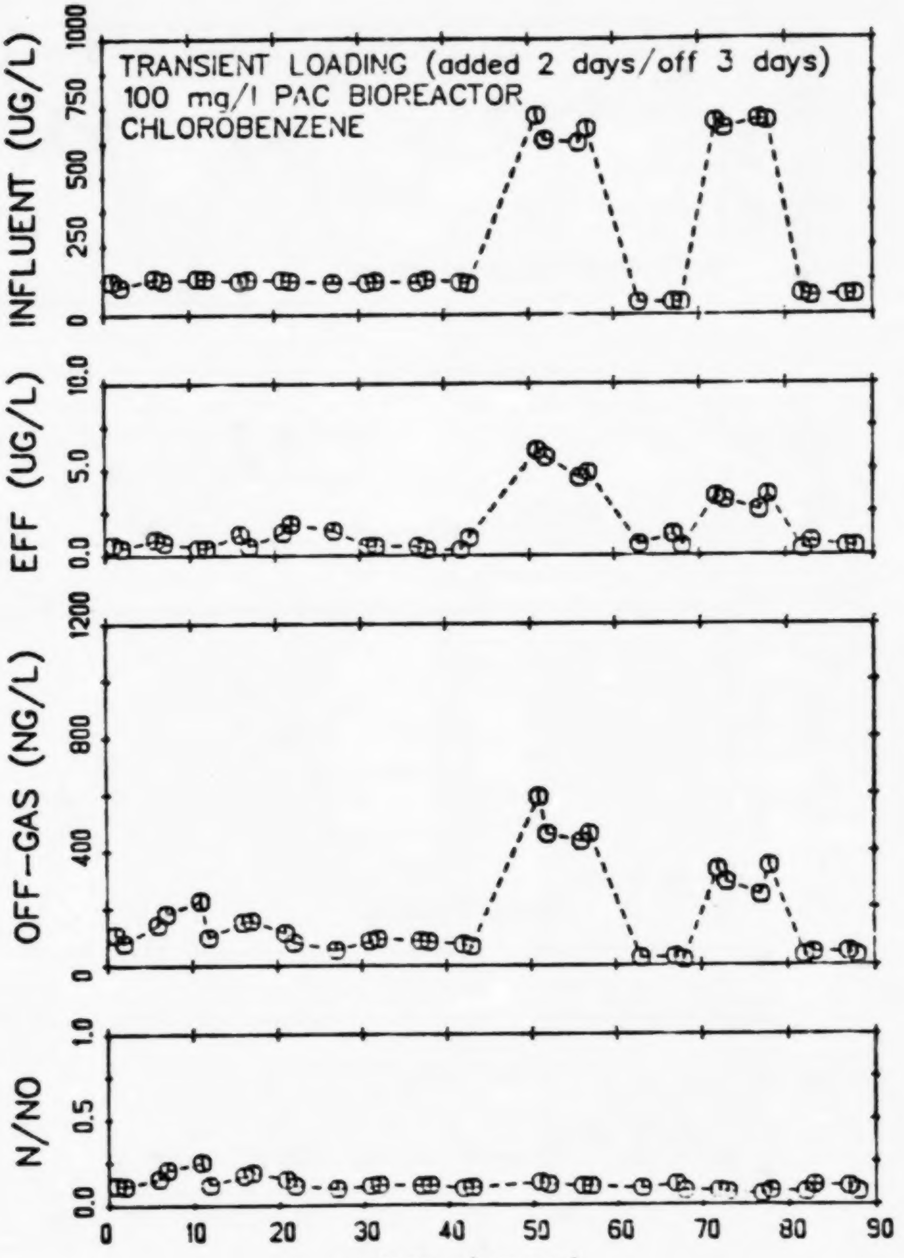


FIGURE 11-82. Chlorobenzene influent, effluent, and off-gas concentrations and fractional recoveries, N/No, measured during a 100 mg/l PAC-bioreactor study with transient toxics loadings. (2 days added/3 days omitted)

TABLE 11-27

RESULTS FOR BENZENE, ETHYLBENZENE, AND CHLOROBENZENE FROM THE 100 mg/ℓ PAC BIOREACTOR OPERATED WITH TRANSIENT INFLUENT TOXICS' LOADINGS (DAYS 21-43)

Parameter	Benzene	Ethylbenzene	Chlorobenzene
Influent	119 (6.6)	107 (6.8)	118 (4.9)
Effluent	0.6 (0.2)	0.8 (0.6)	0.8 (0.5)
Off-Gas	134 (16.8)	128 (20.6)	77 (13.2)
N/N_o	0.164 (0.012)	0.176 (0.027)	0.101 (0.009)
Overall Removal (%)	83.6 (1.2)	82.4 (2.7)	89.9 (0.9)
Reduction in Aqueous Conc. (%)	99.5 (0.2)	99.3 (0.5)	99.3 (0.5)

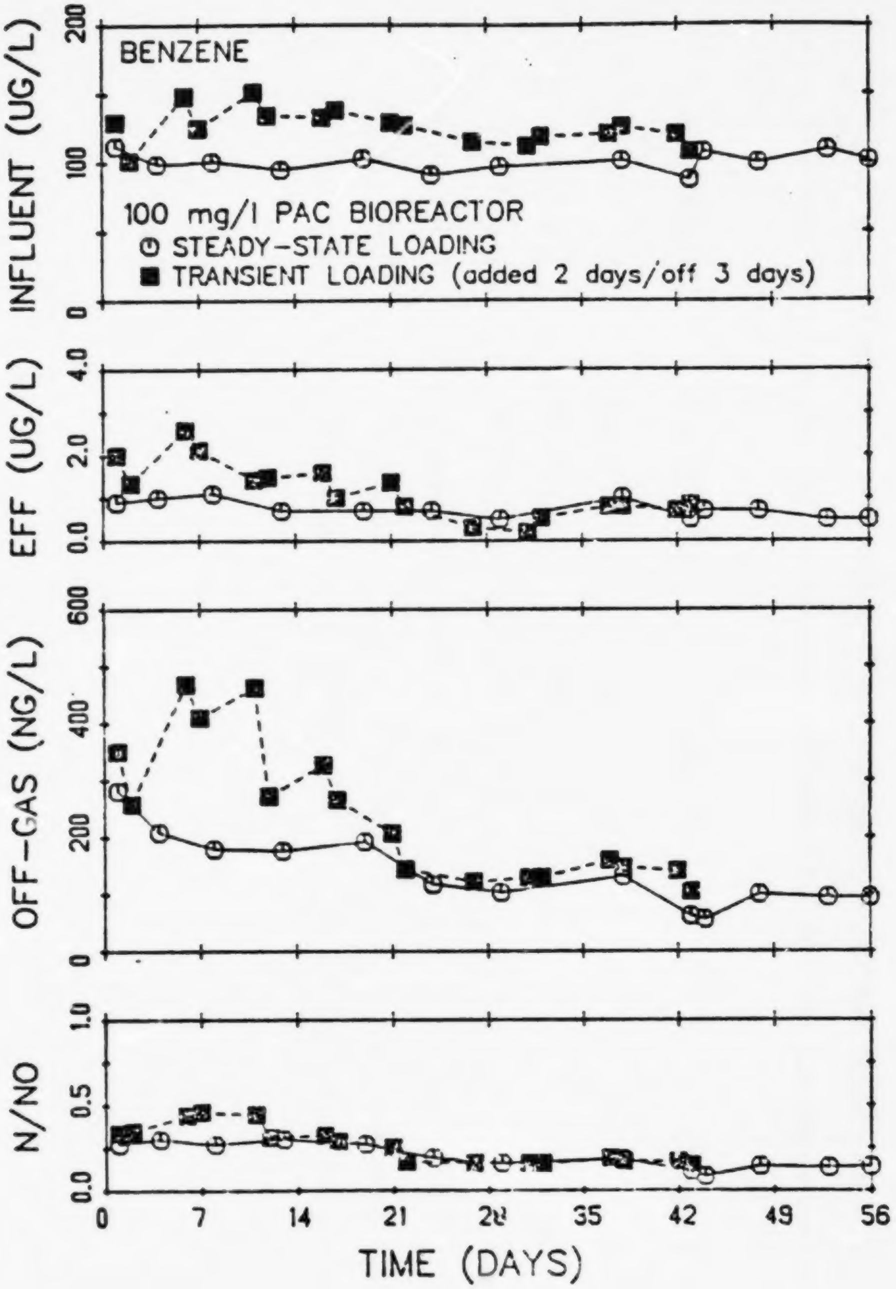


FIGURE 11-83. Comparison of benzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during 100 mg/l PAC-bioreactor studies with steady-state and transient (added 2 days/omitted 3 days) toxics addition to influent.

respectively, during the three week operating period from Day 21 to Day 43. An average influent concentration of 107 ug/l was recorded during that time. As shown by the similarities in N/N_o values in Figure 11-84 overall ethylbenzene removal in the transient loading unit was the same as measured in the steady-state loading bioreactor. Overall steady-state ethylbenzene removals in the steady-state and transient loading units averaged after the initial 21 days to ensure complete acclimation by the activated sludge were 87% and 82%, respectively.

The results for chlorobenzene plotted in Figure 11-82 indicate that despite the transient loading conditions, steady-state chlorobenzene removal was obtained within 24 hours after slurried PAC and chlorobenzene were first added to the reactors. Influent, effluent, and off-gas concentrations averaged 118 ug/l, 0.8 ug/l, and 77 ng/l, respectively, during the 21-43 days of the transient loading study. These results were not significantly different from those recorded for the 100 mg/l PAC bioreactor study with a continuous influent flux of chlorobenzene, as shown by results from the two studies plotted in Figure 11-85. Overall chlorobenzene removals averaged during Days 1 to 43 of the transient loading study and Days 1 to 56 of the steady-state loading study were both 87%.

In summary, there was no significant difference in overall removals measured in 100 mg/l PAC bioreactors operated under conditions of continuous and transient loadings of the three volatile, biodegradable organic compounds. The following relative order of overall removal was observed in both continuous and transient toxics addition:

chlorobenzene > ethylbenzene ≃ benzene

This order of toxics removal is evidenced in the comparative plot of benzene, ethylbenzene, and chlorobenzene overall removals in Figure 11-86 for the 88 days of the transient loading study.

Results presented for bioreactors receiving continuous additions of toxic organic compounds indicated that the addition of 100 mg/l PAC had no significant effect on benzene removal and produced only slight increases in ethylbenzene and chlorobenzene overall removals compared to control units with identical operating conditions. One of the primary objectives of the transient loading study was to determine whether or not PAC addition to activated sludge provided enhanced removals of biodegradable compounds under conditions such as transient toxics loadings which might adversely affect microbial acclimation and biodegradation processes. The effect on toxics removals of PAC-addition to activated sludge systems receiving transient toxics loadings was evaluated by comparing results from the 100 mg/l PAC bioreactor to results from the control activated sludge unit detailed in Section 10. The two bioreactors were operated with identical toxics loading cycles consisting of two days of toxics addition to the influent followed by three days during which time no toxics were added to the influents. Only Days 0 to 43 of the 100 mg/l PAC study were used in the comparison because after Day 43 the influent concentration was varied from approximately 30 to 800 μg/ℓ.

The effect on benzene removal of adding a 100 mg/l PAC dose to activated sludge is shown by the comparison of data from control and

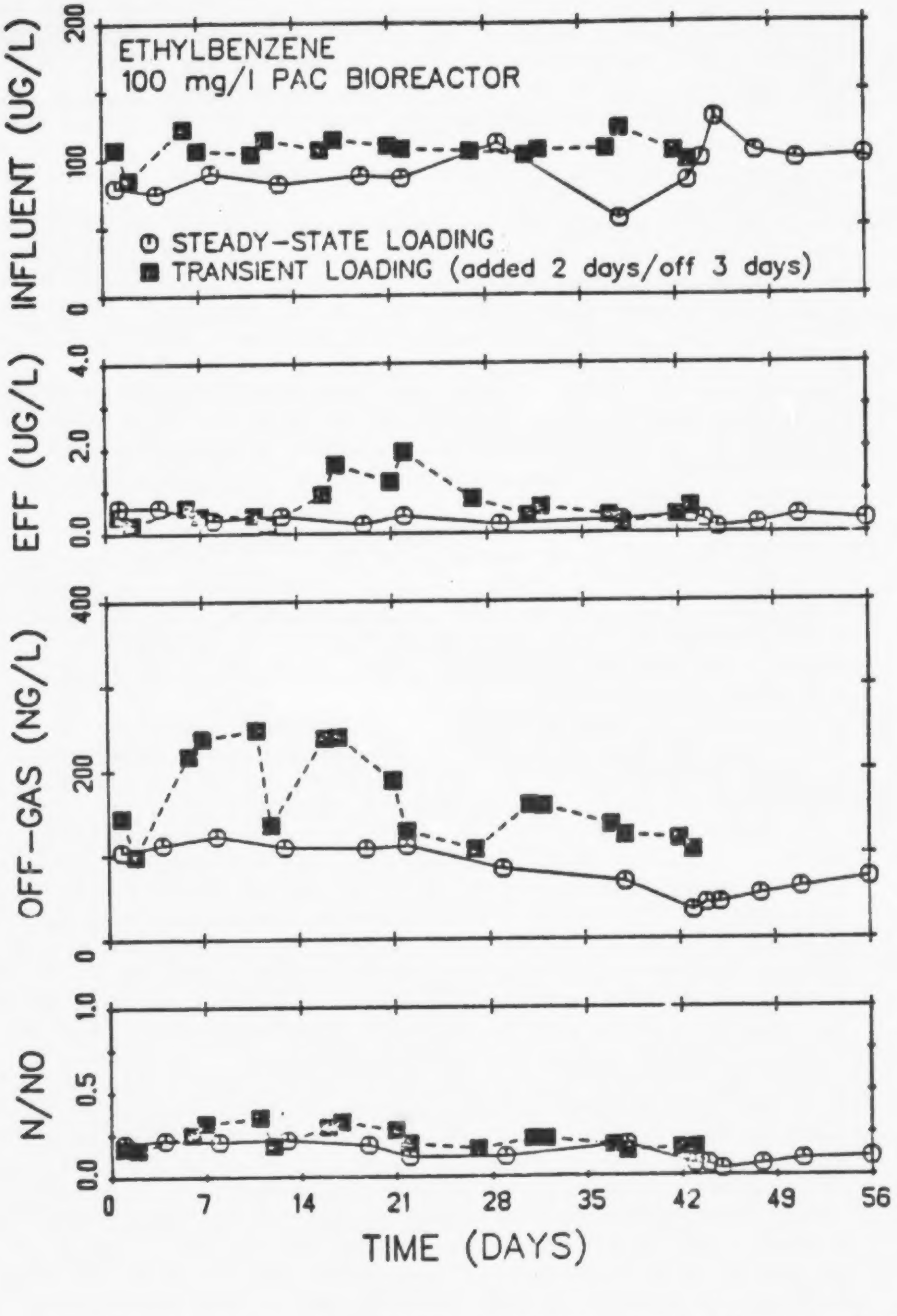


FIGURE 11-84. Comparison of ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during 100 mg/l PAC-bioreactor studies with steady-state and transient (added 2 days/omitted 3 days) toxics addition to the influent.

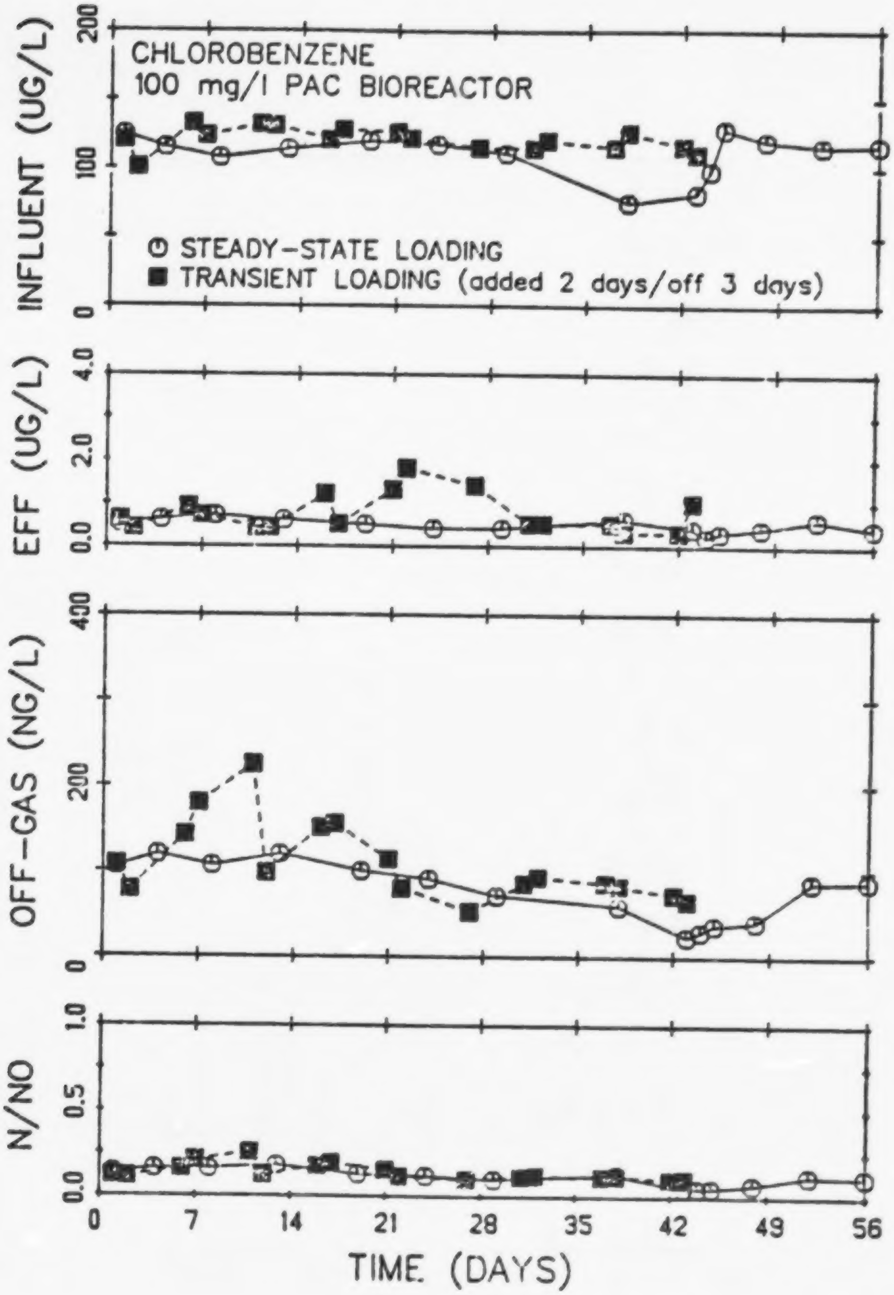


FIGURE 11-85. Comparison of chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during 100 mg/l PAC-bioreactor studies with steady-state and transient (added 2 days/omitted 3 days) toxics addition to the influent.

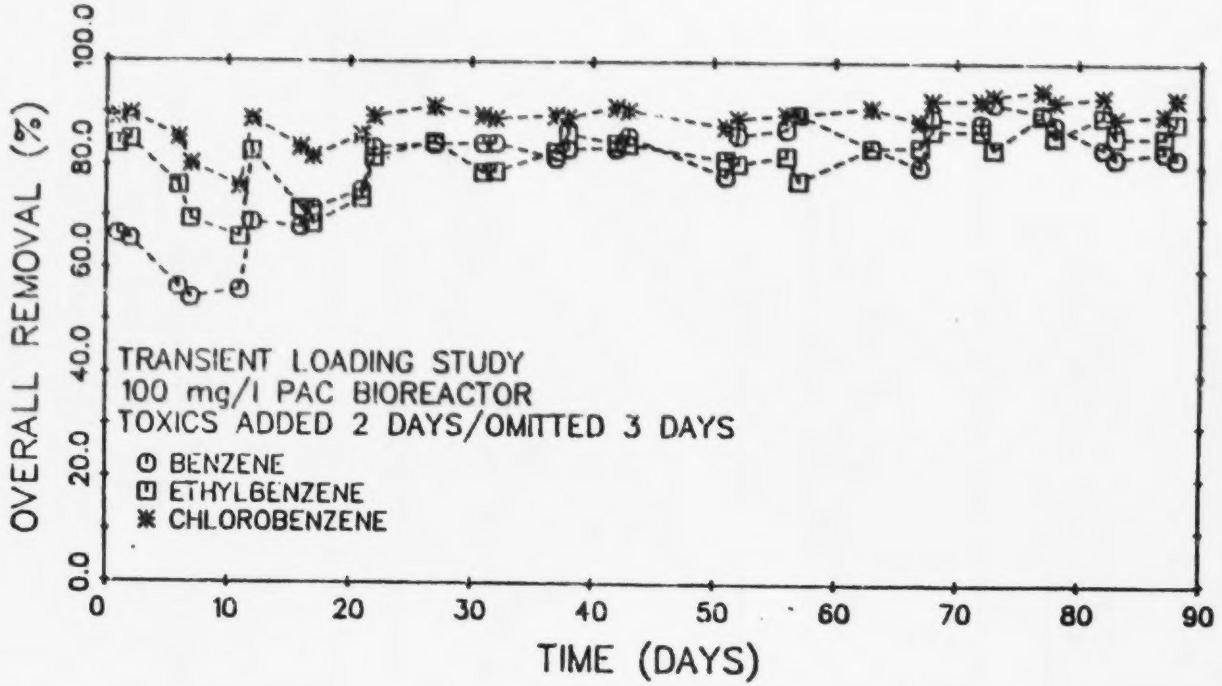


FIGURE 11-86. Comparison of benzene, ethylbenzene, and chlorobenzene overall removals due to biodegradation and adsorption during the 100 mg/l PAC-bioreactor study with transient toxics loadings.

100 mg/l bioreactors in Figures 11-87 and 11-88 and Table 11-28. Influent, effluent, and off-gas benzene concentrations along with N/N_o values for the two studies have been plotted in Figure 11-87. Overall removals have been compared in the plot in Figure 11-88. As the results summarized in Table 11-28 indicate, during periods of steady-state benzene removal there was no difference in overall removals between the control reactor and the unit receiving 100 mg/l PAC. In each unit benzene removal averaged 84% and effluent and off-gas concentrations were approximately 0.5 ug/l and 130 ng/l, respectively.

The addition of 100 mg/l PAC to the transient loading bioreactor did effect a small increase in benzene removal during the acclimation phase. The acclimation phase in the 100 mg/l PAC unit was 21 days compared to nearly 35 days in the control activated sludge bioreactor. As shown by the results in Figure 11-88, the overall removal during the acclimation phase in the PAC bioreactor was consistently greater than that observed during the acclimation phase in the activated sludge unit. When results from the acclimation phases were combined with results from the steady-state periods, overall benzene removal in the 100 mg/l PAC unit averaged 73% compared to 66% in the control activated sludge unit.

Results for ethylbenzene in the 100 mg/l PAC bioreactor have been compared with those from the activated sludge unit in Figures 11-89 and 11-90. Influent, effluent, and off-gas concentrations and N/N_o values from the two studies are shown in Figure 11-89 while overall removals are compared in Figure 11-90. The 100 mg/l PAC bioreactor produced lower effluent and off-gas ethylbenzene concentrations than the activated sludge unit throughout the study. As illustrated by Figure 11-89, while overall ethylbenzene removals gradually increased from less than 20% to nearly 80% in the control unit during the initial four weeks, the overall removal observed in the 100 mg/l PAC unit remained relatively constant and averaged nearly 79%. The PAC unit was not subject to the wide variations in ethylbenzene removal that occurred in the activated sludge bioreactor. Steady-state ethylbenzene removal occurred within 24 hours in the bioreactor receiving 100 mg/l PAC, but was not achieved in the activated sludge unit during the time frame studied.

The most significant difference in toxics removal between the 100 mg/l PAC bioreactor and the control activated sludge bioreactor was observed for chlorobenzene. Effluent and off-gas concentrations and N/N_o values from the two bioreactors have been compared in Figure 11-91 and overall removals have been compared in Figure 11-92. As the results in Figure 11-91 indicate, effluent and off-gas concentrations from the bioreactor receiving 100 mg/l PAC were significantly smaller than those measured in the activated sludge bioreactor between Days 1 and 43. Influent concentrations from the activated sludge and 100 mg/l PAC unit were approximately the same and averaged 118 ug/l and 120 ug/l, respectively. Overall chlorobenzene removal in the activated sludge bioreactor began at 25% on Day 1 and gradually increased to 75% by Day 43. The addition of a 100 mg/l PAC dose to activated sludge produced steady-state removals of nearly 90% by Day 1 of the study, as shown by Figure 11-92, and averaged 89%.

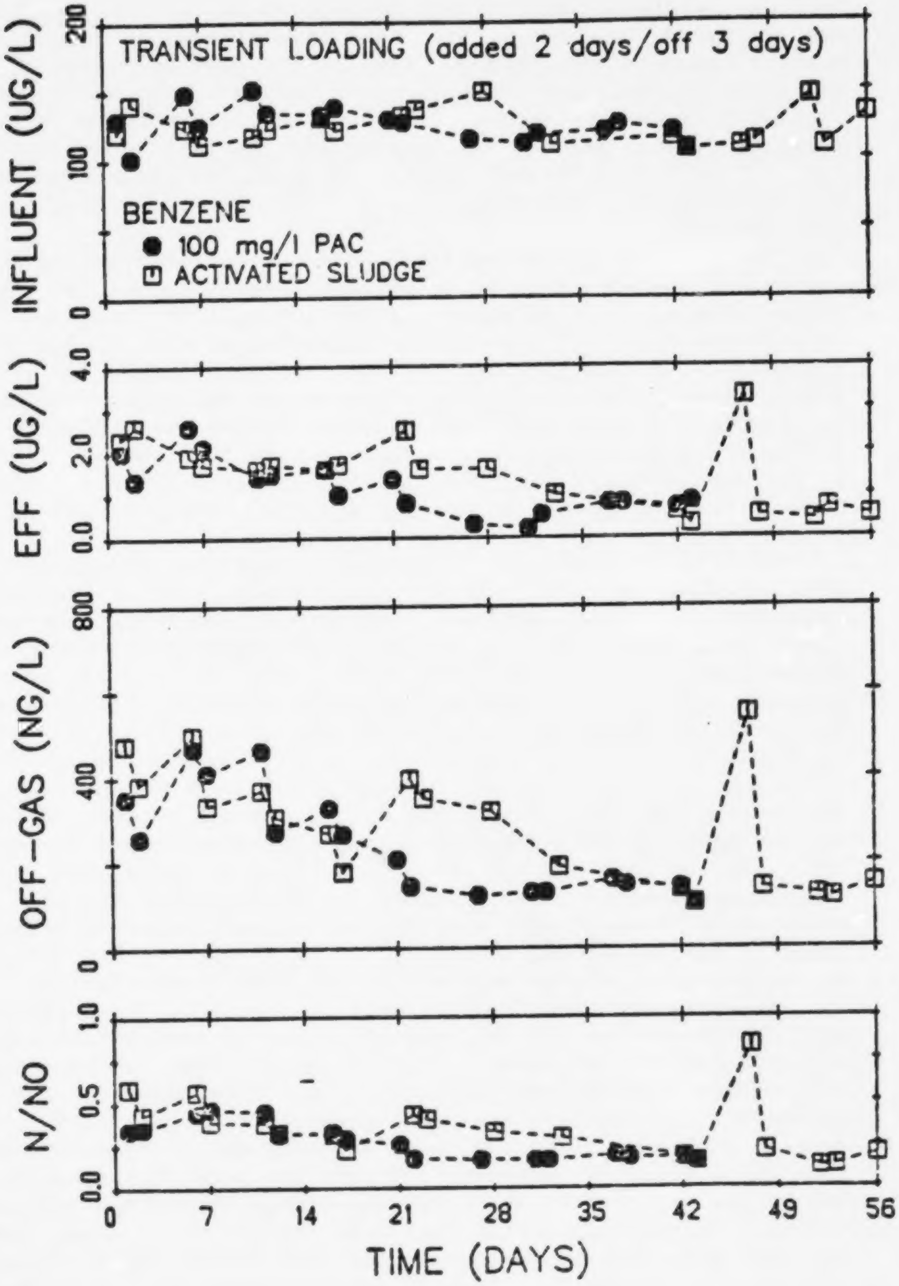


FIGURE 11-87. Effect of a 100 mg/l influent PAC dose on benzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during transient toxics loading studies.

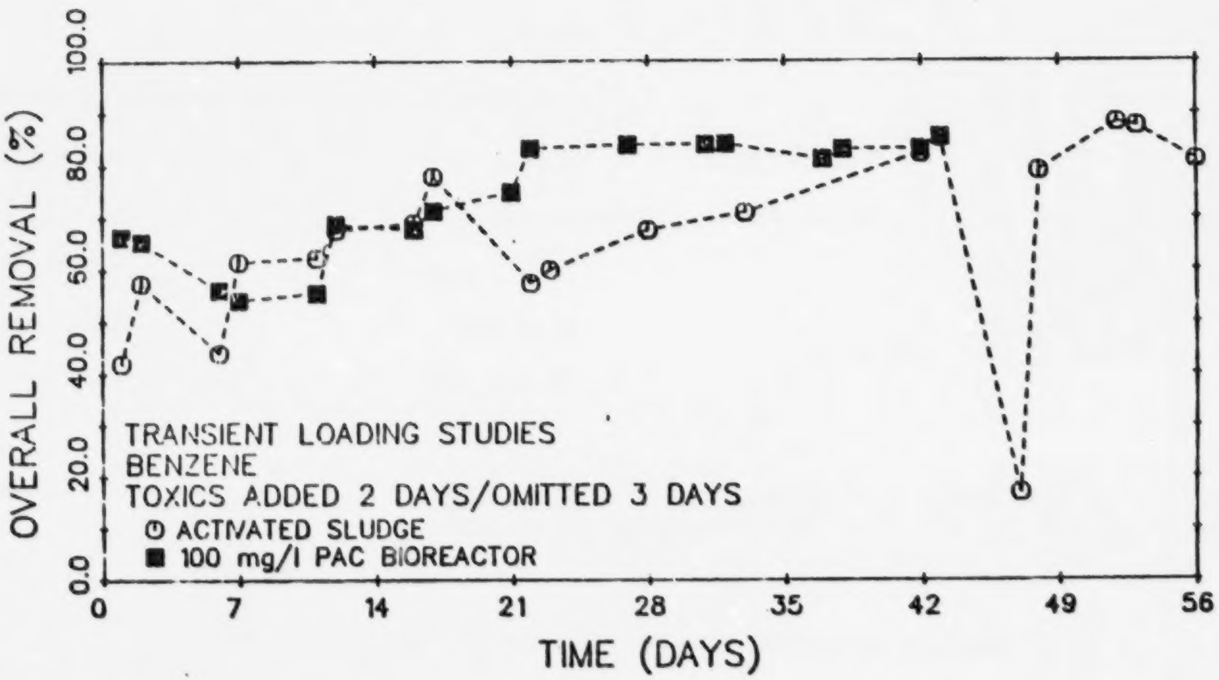


FIGURE 11-88. Effect of a 100 mg/l influent PAC dose on benzene overall removals measured during transient toxics loading studies.

TABLE 11-28

COMPARISON OF BENZENE REMOVAL IN CONTROL ACTIVATED SLUDGE AND 100 mg/ℓ PAC BIOREACTORS OPERATED UNDER TRANSIENT TOXICS LOADINGS

Parameter	Activated Sludge Bioreactor Days 35-57+	 Days 0-56	100 mg/l PAC Bioreactor Days 21-43	 Days 0-43
Influent (ug/l)	121 (15.4)		119	
Effluent (ug/l)	0.5 (0.1)		0.6	
Off-Gas (ng/l)	129 (16.4)		134	
N/N_o	0.161 (0.037)	0.338 (0.18)	0.164	0.266 (0.112)
Overall Removal (%)	83.9 (3.7)	66.2 (18.0)	83.6	73.4 (11.2)
Reduction in Aqueous Conc. (%)	99.6 (0.2)		99.5	

+ Data from pH-induced upset on Day 47 omitted.

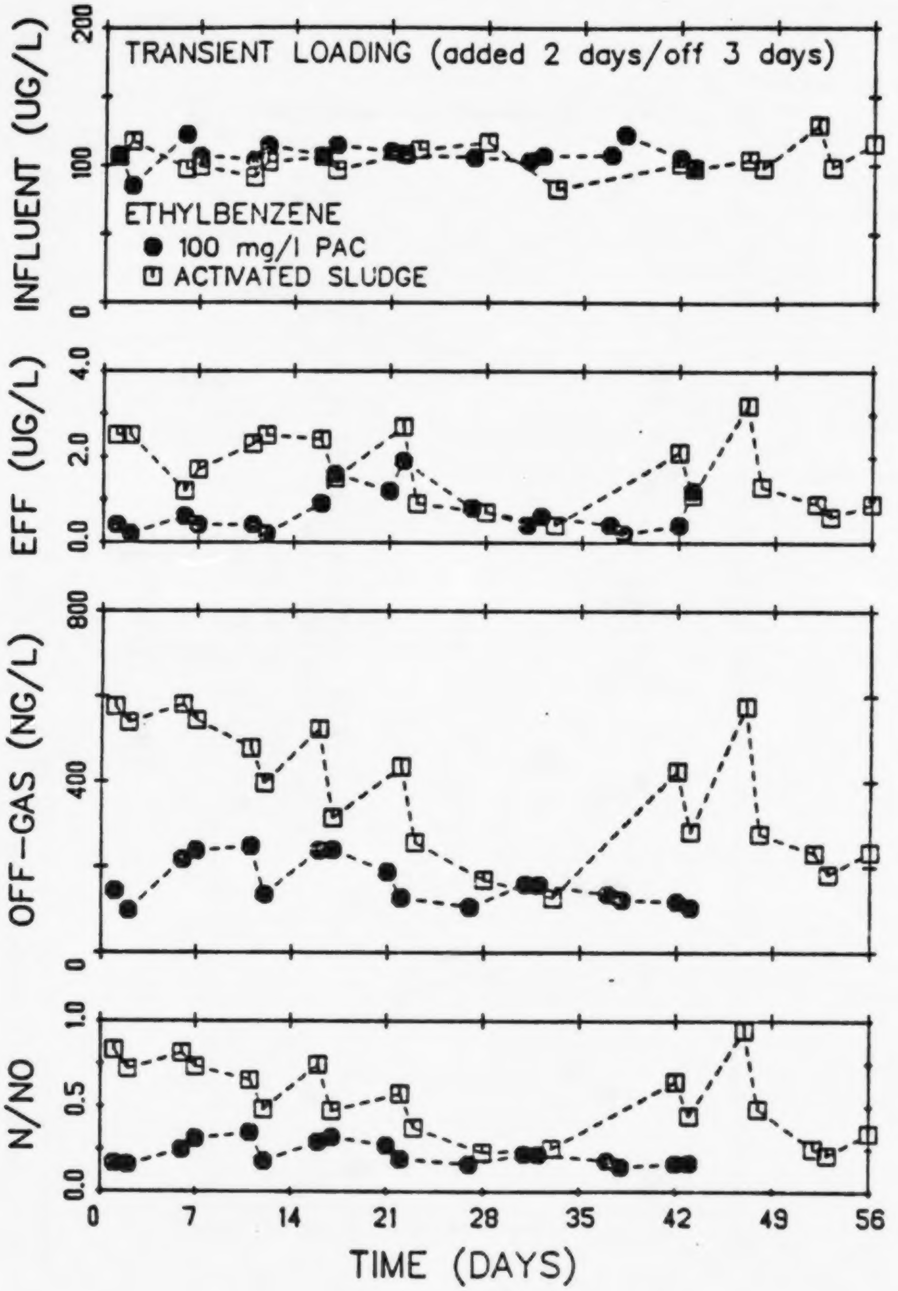


FIGURE 11-89. Effect of a 100 mg/l influent PAC dose on ethylbenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during transient toxics loading studies.

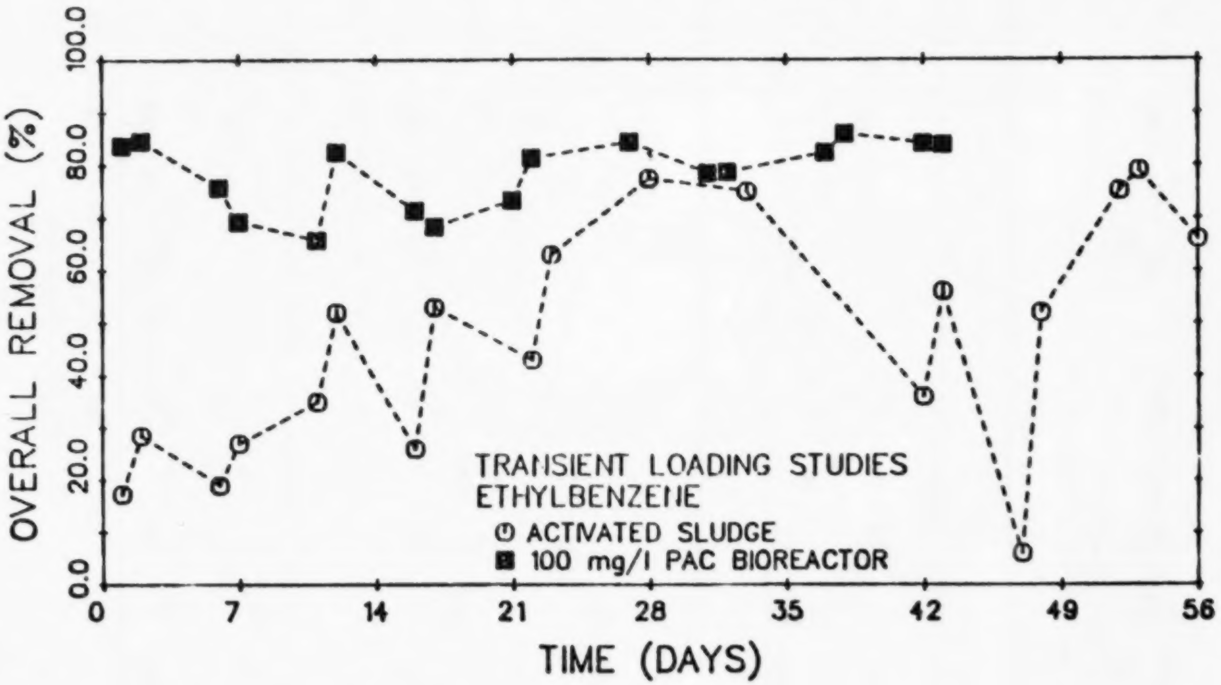


FIGURE 11-90. Effect of a 100 mg/l influent PAC dose on overall ethylbenzene removals measured during transient toxics loading studies.

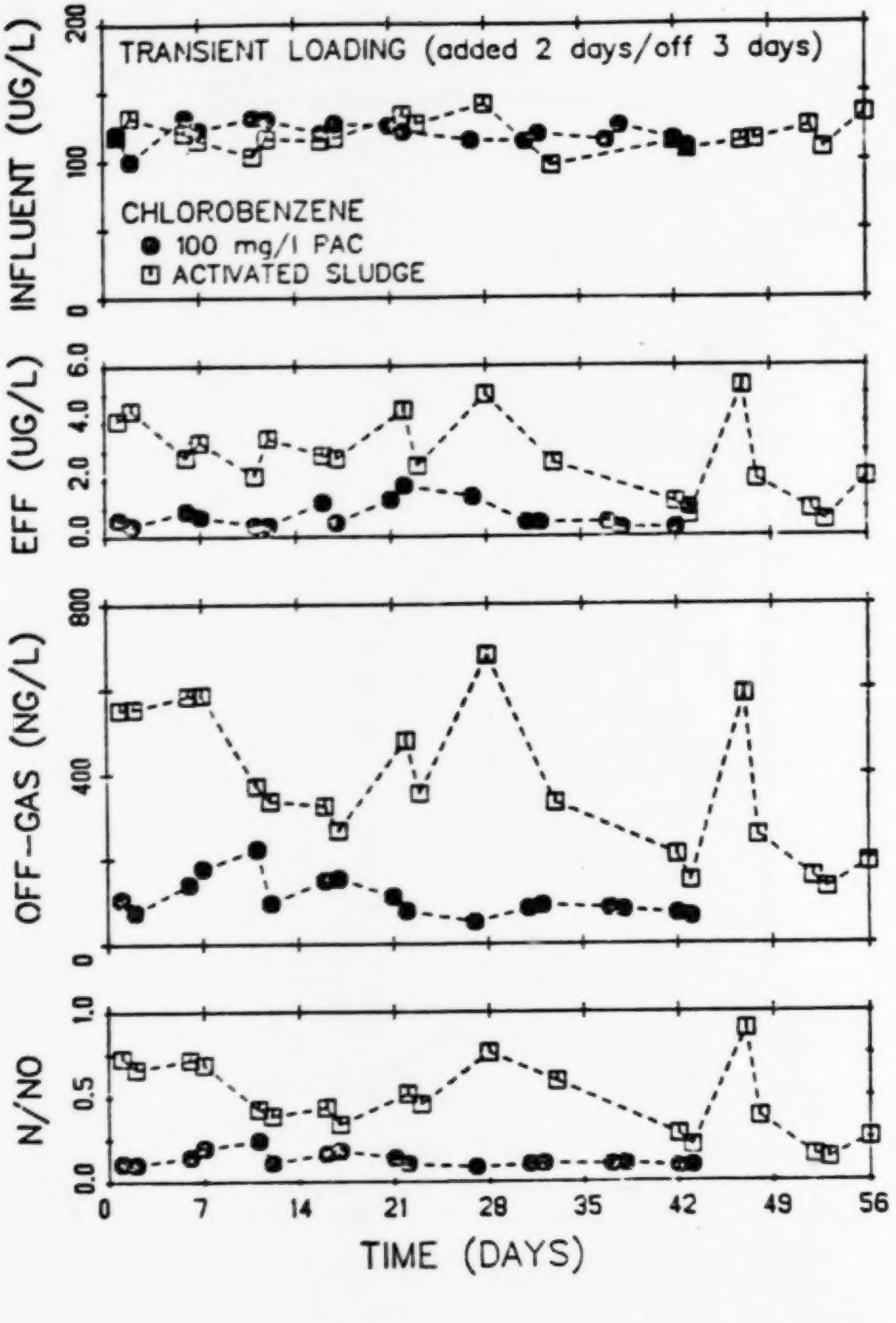


FIGURE 11-91. Effect of a 100 mg/l influent PAC dose on chlorobenzene effluent and off-gas concentrations and fractional recoveries, N/No, measured during transient toxics loadings studies.

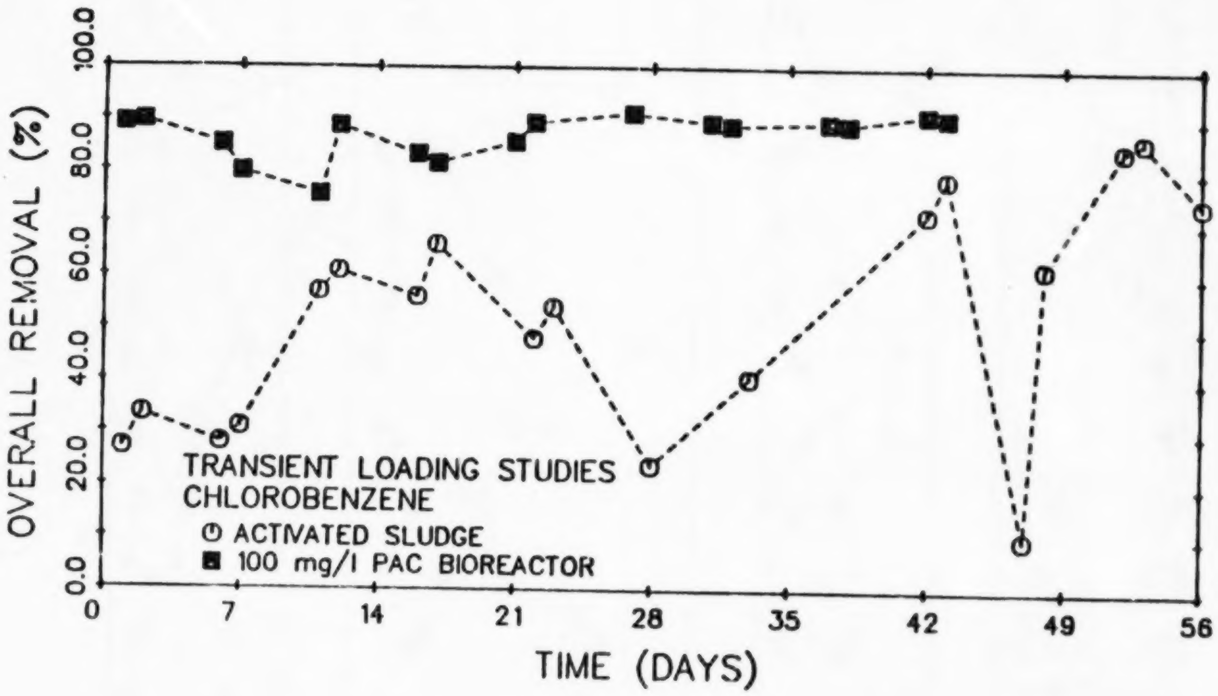


FIGURE 11-92. Effect of a 100 mg/l influent PAC dose on overall chlorobenzene removals measured during transient toxics loading studies.

The most significant benefit to accrue from the addition of 100 mg/l PAC to an activated sludge system receiving transient toxics loadings was an enhanced removal of chlorobenzene, ethylbenzene, and to a lesser extent benzene during the microbial acclimation phase. The improved removals realized on Day 1 gradually diminished as microbial degradation effected increasingly larger overall removals in the control activated sludge unit. The difference in bioreactor performance with respect to toxics removals after the initial four weeks was significant for only chlorobenzene. While the largest chlorobenzene and ethylbenzene removals in the control reactor approached the average values recorded for the PAC unit, the duration of that level of removal in the activated sludge reactor was short. Chlorobenzene and ethylbenzene removals in the activated sludge bioreactor never achieved steady-state levels, but instead were subject to wide fluctuations. The removal of these compounds in the PAC unit, however, was constant throughout the study and steady-state levels were achieved within 24 hours. Therefore, an additional benefit of PAC addition was increased activated sludge performance with respect to toxics removals. In general the less biodegradable and more adsorbable a compound, the greater the benefit of PAC-addition to activated sludge systems experiencing transient loadings of toxic organic compounds.

Following the toxics addition period of Days 0 to 43, the three compounds were not added to the influent again until Day 51, eight days later. On Day 51 the influent concentrations of the toxic compounds were increased from previous steady-state levels of 120 ug/l to between 610 ug/l and 730 ug/l. During the final 37 days of the transient loading study, Days 51 to 88, the influent concentrations during the toxics addition periods were varied from 35 ug/l to 730 ug/l, as shown by Table 11-29. Three days during which time no toxics were added to the influent separated each two day period of toxics addition. Influent, effluent, and off-gas concentrations for each compound from Days 51 to 88 were included in Figures 11-80 to 11-82. Average influent, effluent, and off-gas concentrations and overall removals observed during each of the eight toxics addition periods have been tabulated in Tables 11-30, 11-31, and 11-32 for benzene, ethylbenzene and chlorobenzene, respectively.

Results for benzene given by Figures 11-80 and 11-86 and Table 11-30 indicated that the increased influent concentrations did not produce an adverse impact on overall benzene removal. In general benzene % removals were slightly greater during the periods of high toxics loadings (influent concentrations from 630 to 730 ug/l) compared with removals during periods of low toxic loadings (influent concentrations 35 to 60 ug/l). Removals averaged 88% when the influent concentration was between 630 and 730 ug/l and 83% when the influent benzene level was between 35 and 60 ug/l. As Figure 11-80 shows, effluent and off-gas concentrations, however, were significantly larger during the toxics addition periods with the largest influent concentrations. The largest effluent and off-gas concentrations, 9.0 ug/l and 1160 ng/l, respectively, were measured on Day 52, approximately 24 hours after the influent concentration was first increased to the 630 to 730 ug/l range. While the influent

TABLE 11-29

AVERAGE INFLUENT TOXICS CONCENTRATIONS DURING DAYS 51 TO 88 OF THE TRANSIENT TOXICS LOADING 100 mg/ℓ PAC BIOREACTOR STUDY

Bioreactor Operating Period	Average Influent Concentration (ug/1) Benzene	Ethylbenzene	Chlorobenzene
Days 51 to 52	730	609	678
53 to 55	0	0	0
56 to 57	696	570	649
58 to 61	0	0	0
62 to 63	37	40	44
64 to 66	0	0	0
67 to 68	35	39	44
69 to 71	0	0	0
72 to 73	724	615	687
74 to 76	0	0	0
77 to 78	628	634	704
79 to 81	0	0	0
82 to 83	57	66	70
84 to 86	0	0	0
87 to 88	53	63	69

TABLE 11-30

BENZENE RESULTS FROM DAYS 51 TO 88 OF THE TRANSIENT TOXICS LOADING 100 mg/ℓ PAC BIOREACTOR STUDY

	Toxics Addition Periods							
Parameter	1 Days 51-52	2 Days 56-57	3 Days 62-63	4 Days 67-68	5 Days 72-73	6 Days 77-78	7 Days 82-83	8 Days 87-88
Influent (ug/l)	730	696	37	35	724	628	57	53
Effluent (ug/l)	7.6	4.5	0.7	0.5	3.7	3.3	0.8	0.6
Off-Gas (ng/l)	896	547	38	33	473	448	63	62
Removal (%)	82	89	83	85	90	89	83	82
Aqueous Reduction (%)	99.0	99.4	98.1	98.6	99.5	99.5	98.6	98.9

concentration was maintained within this range for two toxics addition periods, effluent and off-gas concentrations continually decreased due to increased microbial degradation of benzene. Mean effluent and off-gas concentrations during the second toxics addition period of high influent concentrations were approximately 40% lower than those observed during the first period of high influent concentrations. Benzene effluent and off-gas concentrations during the final two periods of high influent concentrations, Days 72-73 and Days 77-78, were relatively constant and nearly 20% lower than the values observed during the second period of high influent concentrations, Days 56-57.

Effluent and off-gas concentrations during the periods of low influent concentrations were consistently lower than the values observed during the high influent concentration periods. During all four low influent concentration periods, average influent concentration was 46 ug/l, the effluent and off-gas concentrations were relatively constant, averaging 0.7 ug/l and 49 ng/l, respectively.

The overall removal of ethylbenzene was relatively unchanged during the periods of high and low influent concentrations as shown by results in Figures 11-81 and 11-86 and Table 11-31. Overall removals corresponding to average influent concentrationsof 607 ug/l (high loading periods) and 52 ug/l (low loading periods) were 83% and 86%, respectively. As was observed for benzene, the effluent and off-gas concentrations during periods of high influent toxics concentrations were significantly larger than those observed during periods of low influent concentrations. Average effluent concentrations during the high influent periods ranged from 3.4 ug/l to 6.2 ug/l, compared to an average value of 0.5 ug/l recorded during the low influent periods. Off-gas concentrations averaged 678 ng/l during the high loading periods and 48 ng/l during the low loading periods. When off-gas fluxes were calculated as a percent of the influent flux, there was no significant difference between the high and low toxics loading periods. In each case the off-gas fluxes represented approximately 15% of the influent fluxes. The effluent flux when evaluated as a percent of the influent flux, likewise, was constant throughout the study, varying from 0.5% to only 1.8%.

Overall chlorobenzene removal during the high and low toxics loading periods was consistently slightly larger than either benzene or ethylbenzene as shown by Figure 11-86. The influent concentration in general had little effect on chlorobenzene removal; it averaged 91% during both high and low toxics loading periods. The influent concentration during the high and low loading periods differed by an order of magnitude and averaged 680 ug/l and 57 ug/l, respectively. (Table 11-32).

The larger influent concentrations did result in more chlorobenzene in the effluent and off-gas than occurred when the influent concentrations were ten times smaller. The largest effluent and off-gas concentrations of 6.2 ug/l and 590 ng/l, respectively were measured on Day 51, Figure 11-82, 24 hours after the initial increase in influent concentrations. Effluent concentrations averaged during the periods of high and the periods of low influent concentrations were 4.2 ug/l and 0.6 ug/l, respectively. Off-gas concentrations during the same operating periods averaged 394 ng/l and 31 ng/l,

TABLE 11-31

ETHYLBENZENE RESULTS FROM DAYS 51 TO 88 OF THE TRANSIENT TOXICS LOADING 100 mg/ℓ PAC BIOREACTOR STUDY

	Toxics Addition Periods							
Parameter	1 Days 51-52	2 Days 56-57	3 Days 62-63	4 Days 67-68	5 Days 72-73	6 Days 77-78	7 Days 82-83	8 Days 87-88
Influent (ug/l)	609	570	40	39	615	634	66	63
Effluent (ug/l)	6.2	5.6	0.4	0.7	5.1	3.4	0.5	0.3
Off-Gas (ng/l)	783	810	44	36	608	510	53	57
Removal (%)	80.6	79.4	83.4	85.2	85.0	87.8	87.6	87.1
Aqueous Reduction (%)	99.0	99.0	99.0	98.2	99.2	99.5	99.2	99.5

TABLE 11-32

CHLOROBENZENE RESULTS FROM DAYS 51 TO 88 OF THE TRANSIENT TOXICS LOADING 100 mg/ℓ PAC BIOREACTOR STUDY

	Toxics Addition Periods							
Parameter	1 Days 51-52	2 Days 56-57	3 Days 62-63	4 Days 67-68	5 Days 72-73	6 Days 77-78	7 Days 82-83	8 Days 87-88
Influent (ug/l)	678	649	44	44	687	704	70	69
Effluent (ug/l)	5.9	4.7	0.6	0.8	3.3	3.0	0.6	0.5
Off-Gas (ng/l)	524	445	23	24	310	294	37	39
Removal (%)	88.2	89.7	91.1	90.6	93.1	93.6	91.3	91.6
Aqueous Reduction (%)	98.9	99.3	98.6	98.2	99.5	99.6	99.1	98.7

respectively. The tenfold differences in average influent concentrations between low and high loading periods resulted in approximate tenfold differences in both effluent concentrations and off-gas concentrations between the two loading periods. When effluent and off-gas fluxes were measured as a percent of the influent fluxes there was no significant difference between low and high toxics loading periods. Off-gas fluxes represented approximately 8% of the influent flux and effluent fluxes were generally less than 2% of the influent flux.

SECTION 12

SUMMARY

The results from this project have provided the first detailed study of the fate and behavior of specific toxic organic pollutants during activated sludge treatment and the integrated activated sludge/carbon treatment process commonly referred to as the PACT® process. This work differed from previous studies of toxic organic compounds in wastewater treatment systems for the following reasons:

1. Individual removal mechanisms of volatilization, biodegradation, and carbon adsorption (integrated activated sludge/carbon treatment studies) were quantified for each compound.

2. Bioreactor off-gases were monitored throughout all bioreactor studies with volatile compounds to quantify the amount of each compound stripped to the atmosphere.

3. Quantification of off-gas fluxes enabled formulation of mass balances for all compounds and a determination of the amounts of each compound biodegraded.

4. Volatilization was sufficiently characterized to enable predictions of steady-state distributions of the compounds between aqueous and gaseous phases that would occur in the absence of biodegradation. Comparisons of predicted and measured effluent and off-gas concentrations showed the effect of biodegradation on the fate of each compound.

5. Influent concentrations in the 50 to 200 ug/l range were typical of actual influent concentrations for municipal and many industrial wastewaters.

For the purpose of summarizing the results from the project, Section 12 will address: (1) results from volatilization and biosorption studies; (2) fate and behavior of toxic organic compounds in activated sludge bioreactors; and, (3) effect of PAC-addition to activated sludge on the fate and behavior of the toxic organic compounds.

12.1 REMOVAL MECHANISMS

Three processes were found to affect the fate and behavior of trace concentrations of toxic organic compounds during activated sludge treatment: (1) volatilization or air-stripping; (2) biosorption by activated sludge mixed liquor suspended solids; and, (3) biodegradation by acclimated activated sludge microorganisms. The addition of PAC provided a fourth removal mechanism, adsorption. Only one of these mechanisms effects ultimate removal of a compound during treatment. Volatilization, biosorption and carbon adsorption act to reduce the aqueous concentration of compounds by redistributing them in the environment, and, therefore, were not considered as ultimate removal mechanisms. Biodegradation results in the disappearance of the parent compound due to its conversion to either a metabolic intermediate, or CO_2 and water. The term removal mechanism refers to any process that effects a reduction in the aqueous concentration of a compound during wastewater treatment. Overall removal or ultimate removal refers to the disappearance of a compound due to biodegradation.

12.1.1 Volatilization

Seven of the nine compounds were found to be readily transferred from the aqueous to gaseous phase in the 10-liter bioreactors. The rate of transfer was modeled as an overall first order process and found to be a linear function of the aeration rate used to provide oxygen to the microorganisms and maintain completely-mixed conditions in the aeration section of the bioreactors. Aeration rates between 3.6 and 4.4 l/min were used in the continuous-flow bioreactor studies. This level was necessary to maintain the mixed liquor suspended solids in suspension. The aeration rate used in the bioreactor studies was larger than that typically used in full-scale treatment facilities and typically produced D.O. levels of 5 to 6 mg/l, two to three times larger than maintained in activated sludge aeration basins. This level of aeration likely effected a greater degree of volatilization of the toxic organic compound than occurs at full-scale activated sludge facilities. The objective of the project was not, however, to simulate typical aeration rates, but to achieve complete mixing using only diffused aeration.

The first order volatilization rate coefficient, k_v, was described by the following equation relating it to the aeration rate in Section 7:

$$k_v = LQ_a + k_{v,o}$$

In the absence of other removal mechanisms, volatilization resulted in rapid reductions in the aqueous concentrations of seven compounds. Table 12-1 compares calculated half-lives for each compound during batch volatilization studies in 10-liter bioreactors with 4.0 l/min aeration rates. The compounds are listed in decreasing order of

TABLE 12-1

COMPUTED HALF-LIFE FOR VOLATILE ORGANIC COMPOUNDS DURING BATCH STRIPPING STUDIES IN 10-LITER BIOREACTORS WITHOUT ACTIVATED SLUDGE

Compound	Half-Life due to Volatilization (min)+ (4.0 l/min Aeration)
Ethylbenzene	8.1
Toluene	8.9
Benzene	9.3
o-Xylene	11.8
Chlorobenzene	14.0
1,2-Dichlorobenzene	27.1
1,2,4-Trichlorobenzene	27.5

+ Half-life $= \frac{-\ln 0.5}{k_v} = \frac{-\ln 0.5}{LQ_a + k_{v,o}}$

volatility, and half-lives range from 8 minutes for ethylbenzene to 27.5 minutes for 1,2,4-trichlorobenzene.

Baseline continuous flow stripping studies, conducted in 10-liter bioreactors without activated sludge, were used to demonstrate the following:

1. Analytical methodologies were sufficient to enable greater than 90% recovery of each compound.

2. Effluent and off-gas concentrations could be predicted from batch measured volatilization rate coefficients, k_v.

3. Off-gas concentrations could be predicted from measured effluent concentrations.

4. Studies conducted with a single compound and up to seven compounds showed that the number of toxics added to the influent had no effect upon either air-stripping or percent recovery of individual compounds.

Volatilization resulted in a 90% reduction in aqueous concentrations of all compounds except lindane and nitrobenzene during the baseline continuous flow studies in bioreactors operated under conditions identical to those used in the activated sludge studies.

12.1.2 Biosorption

The three most hydrophobic compounds, based upon octanol/water partition coefficients, were tested for their ability to accumulate in the mixed liquor suspended solids: 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane. Results from sorption isotherm studies showed that biosorption could be described by the linear sorption model:

$$q_e = K_B C_e$$

Values of K_B for 1,2-dichlorobenzene, lindane, and 1,2,4-trichlorobenzene were 252, 560, and 1025, respectively. When incorporated into a CMF reactor mass balance that included volatilization, biosorption did not significantly change the predicted effluent off-gas concentrations of the two volatile compounds. The model did predict a slight reduction in the aqueous concentration of lindane. Measured effluent and off-gas concentrations were in agreement with predicted values for all three compounds.

12.2 ACTIVATED SLUDGE CMF BIOREACTOR STUDIES

Completely-mixed flow bioreactor studies were conducted in the 10-liter experimental bioreactors equipped with air-tight lids to determine the fate of each compound during activated sludge treatment.

Influent, effluent, and off-gas concentrations were measured every three to four days during all activated sludge studies while waste sludge concentrations of selected compounds were measured less frequently. The use of air-tight lids to enable collection and analyses of the volatile compounds in bioreactor off-gases was a unique and important feature of the experimental system. Influent, effluent, and off-gas fluxes were used to develop mass balances for each compound and determine its fate in the activated sludge system. Baseline studies conducted in 10-liter bioreactors without activated sludge demonstrated that recoveries, (effluent flux + off-gas flux)/(influent flux) x 100, for all compounds, including the most volatile ones, averaged greater than 90%.

Biodegradation was identified by comparing the total flux out of the bioreactors (effluent and off-gas) to the influent flux. Baseline studies demonstrated that the ratio of the mass flux leaving a bioreactor to the mass flux entering it, the fractional recovery or N/N_O, averaged greater than 0.90. Thus N/N_O values significantly less than 0.90 were evidence of biodegradation. Complete recoveries, N/N_O values 0.90, of biodegradable compounds occurred when sufficient quantities of silver chloride or concentrated HCl were added to the influent to inhibit biological activity. Batch biodegradation rate studies were conducted with activated sludge from acclimated bioreactors to confirm that biodegradation was occurring in the continuous flow units.

The activated sludge bioreactor studies were divided into four phases:

1. Single solute: only one toxic organic compound was added to a bioreactor influent.

2. Multi-solute: two to seven compounds were added to a bioreactor influent.

3. Effect of Influent Concentration: effect on biodegradation of influent concentrations from 25 to over 5000 ug/l.

4. Transient Loadings: effect of transient loading conditions on biodegradation of trace toxic organics.

Significant results from each phase of the activated sludge studies have been summarized in the following sections.

12.2.1 Single Solute Studies

1. Table 12-2 gives a summary of the fate of each compound during activated sludge treatment in the 10-liter bioreactors with air-tight lids.

2. Based upon amounts of each compound removed by biodegradation the nine compounds can be divided into the following three

TABLE 12-2

FATE OF TOXIC ORGANICS IN ACCLIMATED ACTIVATED SLUDGE BIOREACTORS OPERATED UNDER STEADY-STATE CONDITIONS

	Percent of Influent			
Compound	Effluent	Off-Gas	Biosorbed	Biodegraded
Benzene	<1	16	0	84
Toluene	<1	17	0	83
Ethylbenzene	<1	22	0	78
O-Xylene	<1	25	0	75
Chlorobenzene	<1	20	0	80
1,2-Dichlorobenzene	6	59	0	35
1,2,4-Trichlorobenzene	10	90	<1	0
Nitrobenzene	2	<1	0	98
Lindane	96	0	4	0

groups. Comparisons of the amounts of the volatile compounds degraded during typical activated sludge studies is given by Figures 12-1 and 12-2.

Biodegradable ($N/N_o < 0.30$)	Poorly-biodegradable ($0.40 < N/N_o < 0.90$)	Non-biodegradable ($N/N_o > 0.90$)
Nitrobenzene	1,2-Dichlorobenzene	1,2,4-Trichlorobenzene
Benzene		Lindane
Toluene		
Chlorobenzene		
Ethylbenzene		
o-Xylene		

3. In general, the amount of a compound biodegraded decreased as the degree of chlorine substitution on the benzene ring increased, as shown by Figure 12-2.

4. Solids retention times from 6 to 12 days had no significant effect on the fate of each compound.

5. Biosorption had no significant effect on the fate of the compounds, except lindane.

6. Biodegradation resulted in reductions in effluent and off-gas concentrations. For volatile compounds, the primary effect of biodegradation was a reduction in off-gas fluxes. Measured as a percent of the amounts predicted to occur in the absence of biodegradation, biodegradation caused approximately the same percent reductions in effluent and off-gas concentrations.

7. Effluent and off-gas concentrations of 1,2,4-Trichlorobenzene were accurately predicted from independently measured volatilization rate coefficients.

8. Off-gas concentrations of all of the volatile compounds, biodegradable and non-biodegradable, were accurately predicted from measured effluent concentrations.

9. Predicted off-gas and measured effluent concentrations could be used to determine the amount of each compound removed by biodegradation.

10. Non-aeration CMB biodegradation studies confirmed the biodegradation observed in CMF 10-liter activated sludge bioreactors.

11. Approximate 14 to 21 day acclimation periods existed prior to steady-state biodegradation of benzene, toluene, ethylbenzene, o-xylene, nitrobenzene, and chlorobenzene.

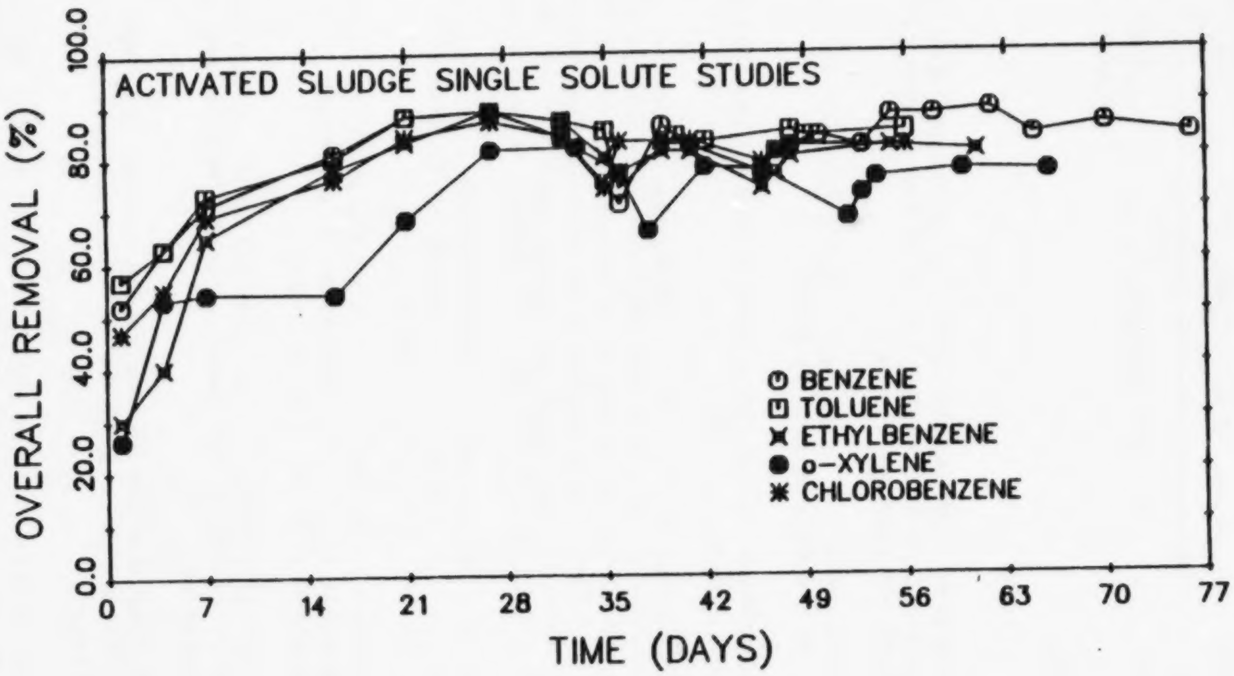


FIGURE 12-1. Comparison of overall removals of volatile toxic organic compounds due to biodegradation during single-solute activated sludge studies.

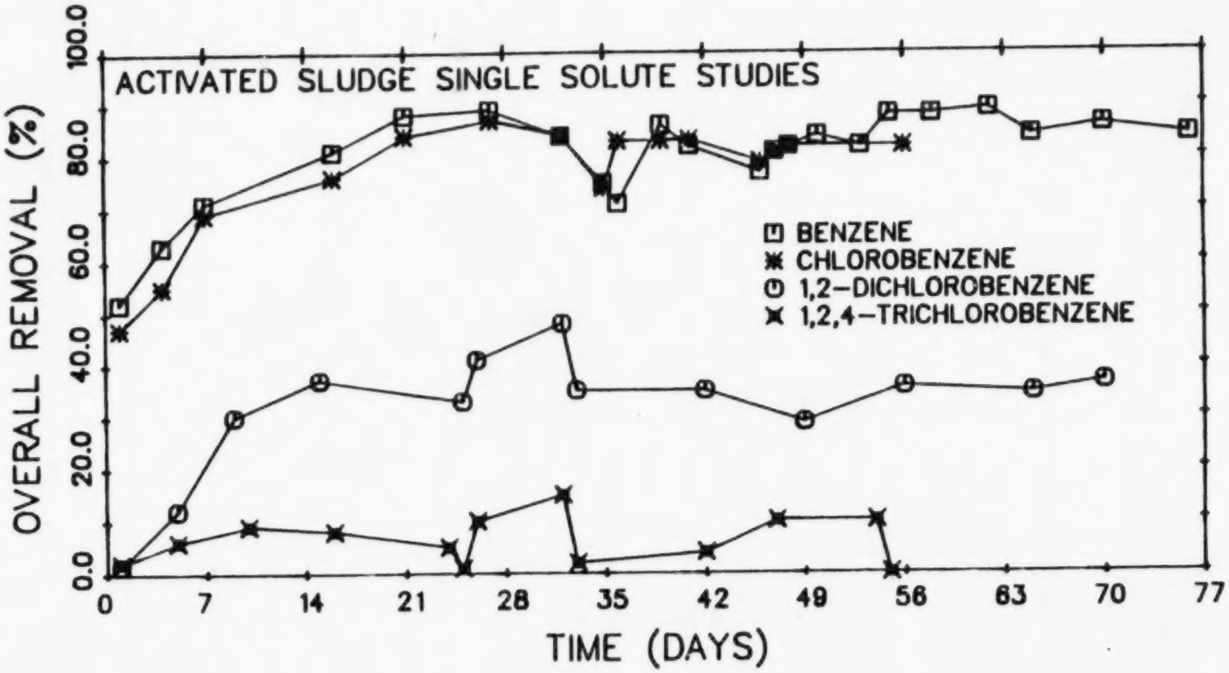


FIGURE 12-2. Effect of increased degree of chlorination of benzene on overall removal due to biodegradation during activated sludge treatment.

12.2.2 Multi-solute Studies

1. The fate of individual toxic organic compounds was the same in bioreactors receiving up to seven toxic organic compounds as occurred in bioreactors receiving only a single toxic organic compound.

2. Recoveries of benzene, toluene, ethylbenzene, o-xylene and chlorobenzene averaged between 15 and 25% in the same bioreactor in which 1,2,4-trichlorobenzene recovery averaged in excess of 90%.

12.2.3 Effect of Influent Concentration

1. Influent concentrations between 50 and 750 ug/l had no effect on the fate of the two non-biodegradable compounds, lindane and 1,2,4-trichlorobenzene.

2. Biodegradation of the three volatile compounds--benzene, ethylbenzene, and chlorobenzene--occurred at influent concentrations as low as 20 and 40 ug/l. Overall removals averaged between 50 and 70%.

3. Percentages of influent benzene, ethylbenzene, and chlorobenzene biodegraded were greater at influent concentrations between 500 and 750 ug/l than occurred at influent concentrations between 20 and 40 ug/l.

4. Simultaneous spike loadings of benzene, ethylbenzene, and chlorobenzene which produced influent concentrations between 6,000 and 10,000 ug/l had no effect on overall bioreactor performance or the biodegradation of toluene and o-xylene, present at influent concentrations between 100 and 200 ug/l. Overall removals of benzene, ethylbenzene, and chlorobenzene increased slightly during the spike loading periods to approximately 90%.

5. Spike loadings of biodegradable compounds producing approximate 10-fold increases in influent concentrations from 100 to 1000 ug/l resulted in only small, temporary increases in effluent and off-gas concentrations.

6. Effluent and off-gas concentrations of individual compounds from bioreactors receiving influent concentrations between 100 and 2000 ug/l were not significantly different indicating an increased amount of biodegradation at the higher concentrations.

7. Inhibition of nitrobenzene degradation and TOC removal occurred at an influent nitrobenzene concentration of approximately 25 mg/l.

12.2.4 Transient Loading Studies

1. An interruption in toxics addition for 2 to 3 days during continuous toxics addition studies had no effect upon biodegradation of benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, and nitrobenzene.

2. A 14-day interruption in the simultaneous addition of benzene, toluene, ethylbenzene, o-xylene, and chlorobenzene to a bioreactor influent resulted in reduced removal due to biodegradation for 2 to 3 days after toxics addition was resumed. After that time period steady-state overall removals resumed.

3. Addition of benzene, ethylbenzene, and chlorobenzene on a cyclic basis of 2 days added to the influent followed by 3 days omitted from the influent had the following effects on biodegradation:

   - Acclimation periods increased from 14 to nearly 42 to 48 days

   - Removals of ethylbenzene and chlorobenzene were less than those observed during continuous toxics addition studies

   - Steady-state removal of benzene approached the same level recorded during continuous toxics addition studies.

4. Increasing the time period toxics were omitted from the influent from 3 to 6 days had no additional effect on biodegradation of benzene, ethylbenzene, and chlorobenzene.

12.3 INTEGRATED ACTIVATED SLUDGE/CARBON TREATMENT BIOREACTOR STUDIES

Integrated activated sludge/carbon treatment studies were conducted in the 10-liter bioreactors with air-tight lids by adding slurried powdered activated carbon (PAC) to the bioreactor. The effect of PAC-addition on overall removals of the toxic organic compounds was evaluted by comparing results from bioreactors receiving PAC to control activated sludge units that did not receive PAC. Influent, effluent, and off-gas concentrations were measured every three to four days during the PAC bioreactor studies. Overall removal in the PAC bioreactor studies was evaluated by comparing the mass flux of a compound out of a bioreactor in the effluent and off-gas combined to influent mass flux. Concentrations of compounds adsorbed to PAC in the mixed liquor were not measured; therefore, there was no way to analytically distinguish between amounts of a compound removed by adsorption and amounts removed by biodegradation. Overall removal in the PAC bioreactor studies refers to the disappearance of a compound due to adsorption and a combination of adsorption and biodegradation for biodegradable compounds.

Results from the integrated activated sludge/carbon treatment studies have been divided into the following sections for the purpose of summarizing the effects of PAC-addition on the removal of the toxic organic compounds:

1. Influent PAC Concentration: effect of influent PAC concentration on the removal of the toxic organic compounds.

2. Solids Retention Time: solids retention times were varied to evaluate the effect of mixed liquor PAC concentration on removal of toxic organic compounds.

3. Multi-solute: two to seven compounds were added simultaneously to influents of bioreactors receiving 50 to 200 mg/l PAC.

4. Effect of PAC Interruption: effect of an interruption in PAC-addition on overall removals of non-biodegradable and biodegradable compounds.

5. Effect of PAC Type: comparison of removals of lindane by three different powdered activated carbons.

6. Effect of Influent Wastewater Composition: lindane removals were evaluated in bioreactors receiving synthetic wastewater and wastewater from the Ann Arbor wastewater treatment facility.

7. Effect of Influent Concentration: effect on overall removals of influent toxics concentrations from 100 to over 1000 ug/l.

8. Transient Loadings: effect of PAC addition on toxics removals in a bioreactor under transient toxics loading conditions.

12.3.1 Influent PAC Dose

1. Table 12-3 gives a summary of the effect of influent PAC doses on the overall removal, defined as biodegradation + carbon adsorption, of the nine toxic organic compounds during integrated treatment in the 10-liter bioreactors with air-tight lids. Results in Table 12-3 were collected during steady-state toxics removal periods.

2. Based on overall removals in Table 12-3 the nine compounds can be divided into the following two groups based on the effectiveness of PAC-addition to activated sludge for providing enhanced toxics removal. These categories represent the effect of PAC-addition on toxics removal during steady-state toxics removal periods and do not reflect the effect of PAC-addition during either acclimation phases or bioreactor upset periods.

TABLE 12-3

AVERAGE OVERALL PERCENT REMOVALS DUE TO BIODEGRADATION AND PAC ADSORPTION MEASURED DURING SINGLE SOLUTE PAC BIOREACTOR STUDIES WITH INFLUENT TOXICS CONCENTRATIONS BETWEEN 100 AND 120 ug/l

		Influent Hydrodarco C Concentration (mg/l)				
Compound	Control	12.5	25	50	100	200
		NON-BIODEGRADABLE				
Lindane	0	68	84	92	ND	ND
1,2,4-Trichlorobenzene	0	ND	69	77	94	94
		POORLY BIODEGRADABLE				
1,2-Dichlorobenzene	36	ND	61	71	93	94
		BIODEGRADABLE				
Benzene	83	ND	79	84	86	86
Toluene	84	ND	ND	ND	ND	90
Ethylbenzene	81	ND	79	85	87	87
o-Xylene	78	ND	ND	82	ND	ND
Chlorobenzene	82	ND	82	85	90	90
Nitrobenzene	97	ND	ND	97	99	ND

ND = Not Determined

PAC-Addition Increased Toxics Removals	PAC-Addition Had Little or No Effect on Toxics Removals
Lindane	Benzene
1,2,4-Trichlorobenzene	Toluene
1,2-Dichlorobenzene	Ethylbenzene
	o-Xylene
	Chlorobenzene
	Nitrobenzene

3. In general, influent PAC doses between 12.5 and 100 mg/l significantly increased the removals of both volatile and non-volatile non-biodegradable and poorly biodegradable compounds. The addition of PAC to activated sludge effected reductions in both off-gas and effluent concentrations. Percent reductions in effluent and off-gas concentrations were approximately the same.

4. The incremental improvement in toxics removal decreased with increasing PAC dose. There was no significant difference in 1,2,4-Trichlorobenzene removal in bioreactors receiving 100 and 200 mg/l PAC.

5. Steady-state removals of non- and poorly-biodegradable compounds was achieved within 24 hours after PAC addition was begun.

6. Influent PAC doses from 25 to 200 mg/l had no significant effect on steady-state effluent and gas concentrations, and therefore steady-state overall removals, of both the volatile and non-volatile biodegradable compounds.

7. The addition of 50 and 100 mg/l PAC did produce improved overall removals of nitrobenzene, chlorobenzene, and ethylbenzene during the initial 14 to 21 day acclimation phases. Improved overall removals were due to reductions in both effluent and off-gas concentrations.

8. Steady-state removals of chlorobenzene and ethylbenzene in bioreactors receiving a 100 mg/l PAC dose occurred within 24 hours after PAC and the toxics were initially added to the influent.

12.3.2 Solids Retention Time (SRT)

1. The influent PAC concentration controlled the steady-state overall removal of non- and poorly-biodegradable compounds and the enhanced removal of some biodegradable compounds during acclimation phases.

2. The accumulation of PAC in the mixed liquor had no effect on the overall removal of any of the toxic organic compounds.

3. Solids retention times ranging from 0.25 to 12 days had no effect on the steady-state removal of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene in bioreactors receiving 50 mg/l PAC. Steady-state mixed liquor PAC concentrations ranged from approximately 50 to 2000 mg/l in bioreactors with 0.25 and 12-day SRT's, respectively.

4. Solids retention times from 0.25 to 15 days had no effect on the steady-state removal of lindane in bioreactors receiving 25 mg/l PAC. Steady-state mixed liquor PAC concentrations ranged from approximately 25 to 1500 mg/l in bioreactors with 0.25 and 15-day SRT's, respectively.

5. Solids retention times from 6 to 12 days had no effect on the steady-state removal of benzene and chlorobenzene in bioreactors receiving 50 mg/l PAC.

12.3.3 Multi-Solute Studies

1. Overall removals of individual toxic organic compounds were the same in bioreactors receiving from three to seven toxic organic compounds as occurred in bioreactors receiving only a single toxic organic compound. Influent toxic concentrations were in the 100 to 300 ug/l range. Multi-solute studies were conducted at influent PAC doses of 50 to 200 mg/l.

2. Spike loadings of selected biodegradable and non-biodegradable compounds resulting in 5 to 10-fold increases in influent concentrations from 100 to 1000 ug/l had no effect on the removal of toxic organics added to influents of multi-solute studies.

12.3.4 Effect of PAC Interruption

1. A 4-week interruption in the addition of 100 mg/l PAC had the following effects on overall removal of volatile toxic organic compounds:

- overall removal of the non-biodegradable compound 1,2,4-trichlorobenzene decreased from 90% to less than 10% in 4 to 5 days

- overall removals of biodegradable compounds benzene, ethylbenzene, and chlorobenzene were not significantly affected indicating the activated sludge was acclimated to these compounds.

2. The continuation of the 100 mg/l PAC dose after the 4-week interruption period had the following effect on overall removals of the toxic organic compounds:

- overall removal of 1,2,4-trichlorobenzene returned to the 90% level within 24 hours
- overall removals of benzene, ethylbenzene, and chlorobenzene were unchanged.

3. Removal of lindane in a bioreactor receiving a 25 mg/l PAC dose decreased from 84% to less than 10% within 6 days after PAC addition was stopped. After 3 days the effluent concentration increased from 12 to >24 μg/ℓ indicating the mixed liquor PAC continued to adsorb lindane for a short time after PAC addition to the influent was stopped.

12.3.5 Effect of PAC Type

1. Approximately the same removal of lindane was recorded in bioreactors receiving the two PAC's recommended for PACT systems, Hydrodarco C and SA-15.

2. The addition of the high surface area experimental PAC PX-21 to activated sludge resulted in greater removals of lindane than occurred with Hydrodarco C or SA-15.

12.3.6 Effect of Influent Wastewater Composition

1. Lindane effluent concentrations from bioreactors receiving Ann Arbor primary effluent as the bioreactor influent were similar to those from parallel operated bioreactors receiving the synthetic wastewater. The influent PAC dose was 30 mg/l.

12.3.7 Effect of Influent Toxics Concentration

1. Increases in influent concentrations of poorly biodegradable and non-biodegradable compounds from 100 to between 1000 and 2000 ug/l resulted in small increases in effluent and off-gas concentrations such that the percent overall removal remained approximately constant.

2. Influent concentrations of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene between 1500 and 2000 ug/l to the same bioreactor which received 50 mg/l PAC resulted in effluent concentrations of only 25 to 30 ug/l.

3. Overall removals of biodegradable compounds increased to greater than 90% when the influent concentrations to a PAC bioreactor receiving 50 mg/l PAC were increased from 100 ug/l to

between 1500 and 2000 ug/l. Increased removal at the higher influent concentration resulted from increased biodegradation rates.

4. No significant variations in steady-state effluent and off-gas concentrations of biodegradable compounds were observed for influent concentrations ranging from approximately 100 ug/l to 4000 ug/l. The influent PAC dose was 50 mg/l.

12.3.8 Transient Toxics Loadings

1. Interruptions in the addition of poorly biodegradable and non-biodegradable compounds to PAC bioreactors had no effect on effluent and off-gas concentrations, and hence overall removals, of those compounds.

2. Two to six day interruptions in the addition of biodegradable compounds had no effect on effluent and off-gas concentrations, and hence overall removals, of those compounds measured 24 hours after the end of the interruption period.

3. Addition of 100 mg/l PAC to a bioreactor receiving transients additions of benzene, ethylbenzene, and chlorobenzene on a cyclic basis of 2 days added to the influent followed by 3 days omitted from the influent had the following effects:

- overall removal of the compounds was the same as observed in single solute continuous toxics addition studies with 100 mg/l PAC doses

- overall removal of benzene was not significantly different than occurred in a control activated sludge unit operated under parallel conditions

- overall removal of ethylbenzene and chlorobenzene was significantly greater in the bioreactor receiving a 100 mg/l PAC dose.

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